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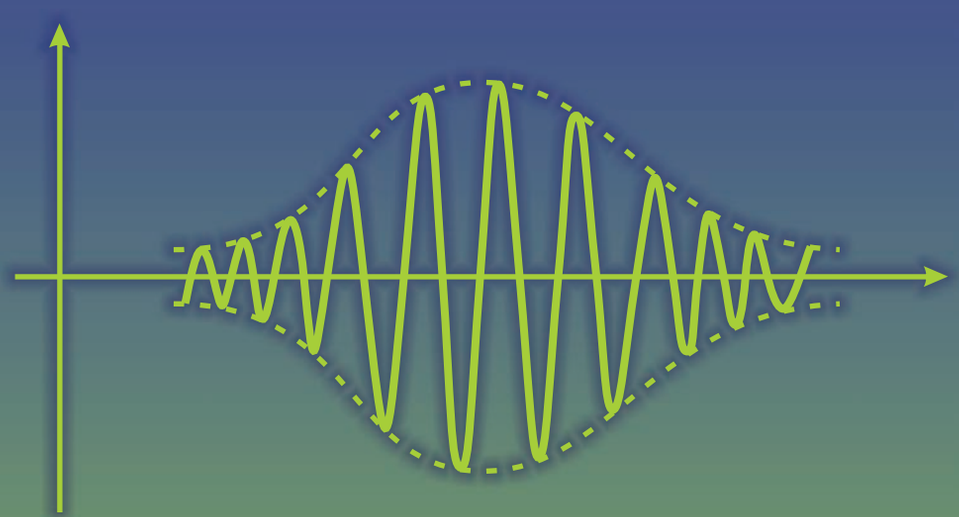
Quantum Mechanics

A Textbook for Undergraduates



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Mahesh C. Jain

QUANTUM MECHANICS

A Textbook for Undergraduates

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PHI Learning Private Limited
New Delhi-110001
2011

QUANTUM MECHANICS: A Textbook for Undergraduates
Mahesh C. Jain

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Dedicated to my late parents

Shri Sham Lal Jain

Smt. Lakshmi Devi Jain

Quantum mechanics is very impressive. But an inner voice tells me that it is not yet the real thing. The theory produces a great deal but hardly brings us closer to the secret of the Old One. I am at all events convinced that He does not play dice.

—Einstein

God not only plays dice. He also sometimes throws the dice where they cannot be seen!

—Stephen Hawking

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Preface

The basic concepts of quantum mechanics constitute the central core around which the whole of modern physics revolves. It is, therefore, natural that a large number of excellent textbooks already exist on Quantum Mechanics. Most of these books provide comprehensive coverage of the material appropriate for the postgraduate courses. Even though these books begin from a basic introduction to quantum theory, the range of topics covered by them is generally broad and large, providing a much deeper coverage of the subject matter. Hence their presentation tends to become complex, both from the viewpoints of mathematical formulation and conceptual discussion. This title, on the other hand, offers a basic introduction to quantum mechanics for students who are exposed to this subject for the first time at the undergraduate level. The first encounter with quantum mechanics is a very thrilling and bewildering experience in which the students realize that the *microscopic* world behaves in a manner which is drastically different from the *macroscopic* world in many ways which are completely beyond their imagination. They learn entirely new concepts which do not conform to everyday experience and to what they have learnt or observed so far. At this beginning stage the students need a book which is easy to understand and takes them along gently through the new concepts and ideas at a pace at which they feel comfortable and can enjoy this marvellous subject. Still, the book should be thoroughly rigorous, giving all the necessary mathematical details so that it can serve as a textbook for the undergraduate curriculum. The present book is written precisely to fulfill this need of the beginner. It has grown out of my interaction (teaching and discussion) with the undergraduate students for more than three decades.

The book is written primarily as a textbook for the students of physics and comprehensively covers the syllabi of all the Indian universities. However, it will also be useful for the students of engineering and chemistry.

I have tried to develop the course in such a manner that the student gets a reasonably good grasp of the fundamental principles and the basic mathematical structure without being unduly frightened. No advanced topics

have been discussed. I have confined the subject matter only to wave mechanics because the other version of quantum mechanics—the matrix mechanics—is not taught at the undergraduate level. It is my personal opinion, too, that matrix mechanics and the state-vector approach should be introduced only after the student has got a reasonably thorough grounding in wave mechanics and its applications to simple systems. It is easier to make a *transition* from the 'classical world' to the 'quantum world' through the more familiar mathematics (differential equations) of wave mechanics than through the abstract algebraic approach, however elegant it may be.

The book is divided into 14 chapters. After a brief historical introduction in Chapter 1, the origin of quantum theory is presented in Chapter 2. Here, it is discussed how Planck explained the blackbody radiation by postulating the quantization of radiant energy and then, how the photoelectric effect and the Compton effect established the particle nature of radiation. Chapter 3 highlights how Bohr explained the structure and spectra of simplest atoms using the quantum hypothesis—by postulating discrete stationary orbits and quantum jumps. This chapter also discusses the Franck–Hertz experiment, which demonstrated directly that the energy is absorbed by atoms in discrete quanta, and explains the correspondence principle, which served as a guiding principle in the initial development of quantum mechanics.

The basic framework of quantum mechanics is developed in Chapters 4, 5 and 6. Beginning with De Broglie's hypothesis, these chapters discuss in detail the need for a wave function and its interpretation, the wave packets, the uncertainty principle, the Schrödinger equation, the operators, the eigenfunctions and eigenvalues, the expectation values, etc. The application of this framework to simple systems—potential wells, barriers and harmonic oscillator—are explained in Chapters 7, 8 and 9. Chapter 10 presents the formal structure of quantum mechanics as a set of seven postulates. In Chapter 11, the quantum mechanical treatment of orbital angular momentum and its application to the rigid rotator are presented.

In Chapters 12, 13, 14 the application of quantum mechanics to the structure of atoms is discussed. Here the Schrödinger equation for a hydrogenic atom is first solved. The concept of spin and its consequences, the Pauli exclusion principle, the atomic shell structure, the coupling schemes and the Zeeman effect are then discussed in detail.

Each chapter contains a number of solved problems and exercises. These are an essential part of the book and must be taken very seriously. A proper understanding of quantum concepts is not possible without undergoing the grilling in problem solving. A set of review questions is also given at the end of each chapter. These are of the type that are generally asked in the examinations. Students are advised to write their answers. This will help them to comprehend the subject faster. Each chapter ends with a summary of all the important key points discussed therein.

Students are advised not to get disheartened if they feel confused while reading certain concepts in the first instance. They should have the patience to read the whole thing again. They can take heart from one of the greatest scientists, R.P. Feynmann, who once remarked, "nobody understands quantum mechanics!" Even if the readers find quantum mechanics conceptually difficult, they will find it beautiful and enjoyable and with persistent effort, will soon acquire a working knowledge appropriate at their level.

I have made all efforts to see that the book is free of errors. However, some might have still remained. I shall be thankful to the students and teachers alike if they point these out to me. Suggestions for the improvement of the book are also welcome.

I express my sincere thanks to the management and staff of Prentice-Hall of India for publishing the book in an excellent form. In particular, I am indebted to Shri Darshan Kumar, Shri Malay Ranjan Parida and Shri K.K. Chaturvedi for taking keen interest in this book and giving valuable suggestions during the course of its production.

Mahesh C. Jain

Chapter

1 Historical Introduction

Quantum mechanics provides the theoretical framework which makes it possible to describe, with reasonably good accuracy, the behaviour of radiation and matter at microscopic (atomic and subatomic) levels. The creation of quantum mechanics is the most outstanding development of modern science. It is like a revolution that has changed the old concepts of reality in many respects. As the great mathematician Henri Poincaré has said:

"*It is hardly necessary to point out how much quantum theory deviates from everything that one has imagined until now; it is, without doubt, the greatest and deepest revolution to which natural philosophy has been subjected since Newton*".

Towards the end of the nineteenth century, physicists had started believing that almost all the fundamental laws of nature have been discovered and as such, the main task of physics is over[†]. Various branches of physics were unified in a general theoretical framework, now called classical physics, and it was felt that all known or to be discovered physical phenomena can be explained in this framework.

The universe consists of two types of entities—matter and radiation. Matter is made up of localized particles. The *classical mechanics*, formulated by Newton and further developed by Hamilton, Lagrange and many others, successfully explained the motion of material particles subjected to various types of forces. Maxwell developed the *electromagnetic theory* in 1855 which combined electricity, magnetism and optics into a single framework. He showed that all radiations, including light, are electromagnetic waves. The existence of such waves was confirmed experimentally by Hertz in 1887. All waves show interference and diffraction phenomena which were well understood theoretically.

During the end of the nineteenth century and the beginning of the twentieth, physicists turned their attention to the study of the microscopic structure of

[†] In fact, when Max Planck entered into physics, he was advised not to study the subject because all the problems had been solved.

matter, the nature of electromagnetic radiation and the interaction of radiation with matter. In these studies a number of experimental results were obtained which could not be explained on the basis of classical physics. These puzzling results created a crisis in theoretical physics. Quantum theory had its origin in the attempts made to explain these results. Radically new concepts were required which were completely incompatible with classical physics. These new concepts are: *the particle nature of radiation, the wave nature of matter and the quantization of physical quantities*.

The originator of the quantum idea was **Max Planck**. He introduced the concept of *quantization of radiant energy* in 1900 to explain the spectral distribution of radiant energy emitted by a heated blackbody. **Einstein** took the next important step in 1905. He used Planck's idea to explain the puzzling features of the photoelectric effect. In 1923, **Compton** explained the change of wavelength of X-rays when they are scattered by free or weakly bound electrons (Compton effect). The works of Einstein and Compton showed that radiation can behave as particles, thus bringing in *wave-particle duality of radiation*.

In 1913, **Niels Bohr** used Planck's quantum hypothesis and gave the first successful theory to explain the stability and observed spectrum of the hydrogen atom. He introduced the *quantization of angular momentum* and the concept of *quantum jumps*.

The next major step was taken by **L. de Broglie** in 1923. He suggested that like radiation, matter also has dual nature, i.e., there is a wave associated with every material particle. The wave nature of electrons was verified by **Davisson and Germer** and independently by **G.P. Thomson** in 1927. In 1926, **Schrödinger** discovered the equation for matter waves and thus formulated *wave mechanics*, which is one form of quantum mechanics. Simultaneously, another version, called *matrix mechanics*, was developed in 1925 by **Heisenberg**, **Born** and **Jordan**. It was later shown that the two versions are equivalent. Wave mechanics is easier to understand intuitively and therefore, the first course in quantum mechanics always starts with this version.

The wave-particle duality of matter led to a very important principle, called the *uncertainty principle*. It was discovered by **Heisenberg** in 1927. Much mystery and controversy surrounded this principle from the beginning. However, it is considered to be a fundamental principal of nature and is indispensable for a complete understanding of the microscopic world.

In order to reconcile the quantum theory with the classical physics, Bohr formulated the *correspondence principle* in 1923. This principle serves as a guide in the development of quantum theory. It requires that the results of quantum theory must become identical with those of classical physics if the dimensions of the system under consideration tend to approach the dimensions of classical systems.

Nobel Awards for the Development of Quantum Theory

1918	Max Planck	Discovery of energy quanta
1921	Albert Einstein	Discovery of the law of photoelectric effect
1922	Niels Bohr	Investigation of the structure of atoms, and of the radiation emanating from them
1923	Robert A. Millikan	Work on the photoelectric effect
1925	James Franck Gustav Hertz	Discovery of the laws governing the impact of an electron on an atom
1927	Arthur H. Compton	Discovery of the effect named after him
1929	Louis de Broglie	Discovery of the wave nature of electrons
1932	Werner Heisenberg	Creation of quantum mechanics
1933	Erwin Schrödinger P.A.M. Dirac	Discovery of the new productive forms of atomic theory
1937	Clinton J. Davisson George P. Thomson	Experimental discovery of the diffraction of electrons by crystals
1945	Wolfgang Pauli	Discovery of the exclusion principle
1954	Max Born	Fundamental research in quantum mechanics, especially for the statistical interpretation of the wave function

Chapter

2

Particle Nature of Radiation: The Origin of Quantum Theory

Chapter Contents

2.1 Blackbody Radiation: Planck's Quantum Hypothesis
2.2 The Photoelectric Effect
2.3 The Compton Effect
2.4 Dual Nature of Radiation

2.1 BLACKBODY RADIATION: PLANCK'S QUANTUM HYPOTHESIS

The quantum theory had its origin in the search for an explanation of the spectral distribution of radiant energy emitted by a blackbody. An ideal blackbody is defined as one that absorbs all electromagnetic radiation incident upon it. It follows from Kirchhoff's law that such a body is also a better radiator of energy, of all frequencies, than any other body at the same temperature. An ideal blackbody does not exist. The nearest approximation is a hollow enclosure having blackened inner walls and a small hole. Any radiation entering the enclosure through the hole will suffer reflections repeatedly and get absorbed inside. There is very little chance of its coming out. If the enclosure is heated to a certain temperature *T*, it emits radiation. In thermal equilibrium, this radiation depends only on *T*. A very small fraction of the radiation will pass out through the hole. Since the hole acts as a blackbody, this radiation is called the *blackbody radiation* at temperature *T*. Figure 1.1 shows the wavelengthwise distribution of the intensity (I_λ) of this radiation. It is found that the radiated energy is maximum at a particular wavelength λ_m and is small for very short and very long wavelengths.

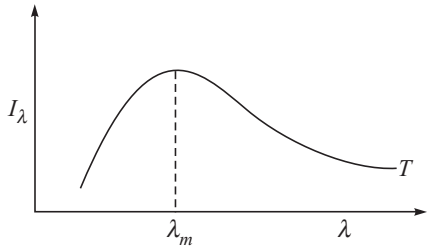

Figure 2.1 Spectral distribution of blackbody radiation.

Various attempts were made to explain the shape of this curve. Wien obtained the following semiempirical formula, known as **Wien's law:**

$$I(\lambda, T) = \frac{ae^{-b/\lambda T}}{\lambda^5} \tag{2.1}$$

where a and b are adjustable parameters. This law fitted the experimental curve fairly well except at long wavelengths. However, it is not satisfactory in the sense that it is not derived from a model which would relate the emitted radiation to physical processes taking place within the enclosure.

A more complete theory was given by Rayleigh and Jeans, based on classical electrodynamics and thermodynamics. They considered the radiating body as a collection of a large number of charged particles performing linear simple harmonic motions. These oscillating charges emit and absorb electromagnetic radiation. At thermal equilibrium, the energy density of the radiation inside the cavity will be equal to the energy density of the atomic oscillators situated in the walls of the cavity.

It can be shown that the number of oscillators per unit volume, of frequency ν, called *Jeans' number*, is

$$n(\nu) = \frac{8\pi\nu^2}{c^3} \tag{2.2}$$

Further, according to the classical theory of equipartition of energy, the average energy of an oscillator at temperature T is kT, where k is Boltzmann's constant. Thus, the energy density of the radiation of frequency ν in the cavity, at temperature T, is

$$U(\nu, T) = \frac{8\pi\nu^2}{c^3} kT \tag{2.3}$$

This is the **Rayleigh-Jeans Law**. It can be stated in term of wavelength λ if we note that

$$n(\lambda)d\lambda = n(\nu)\,d\nu$$

or

$$n(\lambda) = n(\nu)\left|\frac{d\nu}{d\lambda}\right|$$

$$= n(\nu)\left|\frac{d}{d\lambda}\left(\frac{c}{\lambda}\right)\right|$$

$$= n(\nu)\frac{c}{\lambda^2}$$

$$= \frac{8\pi}{c^3}\left(\frac{c^2}{\lambda^2}\right)\left(\frac{c}{\lambda^2}\right)$$

$$= \frac{8\pi}{\lambda^4}$$

Thus,

$$\boxed{U(\lambda, T) = \frac{8\pi}{\lambda^4} kT} \tag{2.4}$$

The intensity $I(\lambda, T)$ of the radiation emitted by the cavity hole is proportional to $U(\lambda, T)$. The exact relation is

$$I(\lambda, T) = \frac{c}{4} U(\lambda, T)$$

where c is the speed of light. Therefore,

$$\boxed{I(\lambda, T) = \frac{8\pi c}{4\lambda^4} kT} \tag{2.5}$$

It is found that the Rayleigh-Jeans law agrees with the experimental results in the long wavelength region. However, it diverges as the wavelength tends to zero. This failure of the Rayleigh-Jeans law is referred to as the "*ultraviolet catastrophe*". Moreover, Equation (2.3) implies that the total energy emitted at all temperatures except absolute zero is infinite:

$$U(T) = \int_0^\infty U(\nu, T) d\nu = \frac{8\pi kT}{c^3} \int_0^\infty \nu^2 d\nu = \infty$$

which is obviously impossible.

Since the law was derived by applying the principles of classical physics rigorously, it gave a serious below to classical physics and suggested that there was something fundamentally wrong with it.

Planck's Radiation Law

Planck realized that some radical change was required to explain the experimentally observed spectrum of blackbody radiation. After much trial, he arrived, in 1900, at the following postulate which is known as **Planck's quantum hypothesis:**

The material oscillators (in the walls of the cavity) can have only discrete energy levels rather than a continuous range of energies as assumed in classical physics. If a particle is oscillating with frequency ν, its energy can take only the values

$$\boxed{\varepsilon_n = nh\nu, \quad n = 0, 1, 2, \ldots} \tag{2.6}$$

where h is a constant, later called the Planck's constant. The quantity hν is called a quantum of energy. This implies that the particle can emit or absorb electromagnetic energy, not continuously in arbitrarily small amounts, but in multiples of the quantum hν.

The value of the constant *h* was chosen to fit the experimental data. Planck obtained the value 6.55×10^{-34} Js, which is close to the presently accepted value 6.625×10^{-34} Js. It is a fundamental constant of nature.

Since the energies of the oscillators are restricted to integral multiples of $h\nu$, the average value of their energies will be different from kT, the value obtained using the classical equipartition theorem. It can be calculated as follows:

Consider all the particles oscillating with frequency ν. At absolute zero, all the oscillators will be in the lowest energy state. At higher temperatures, some of the oscillators are excited to higher states. At temperature T, in equilibrium, the number of oscillators with energy ε_n is given by the Maxwell-Boltzmann function

$$N(n) = N_0 e^{-\varepsilon_n/kT}$$

This shows that higher the energy state, less likely is it to be populated. As $n \to \infty$, $N(n) \to 0$. Note that in classical theory, oscillators of all energies are excited with equal probability.

The average energy per oscillator is

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty} N(n)\varepsilon_n}{\sum_{n=0}^{\infty} N(n)}$$

$$= \frac{\sum_{n=0}^{\infty} N_0 e^{-nh\nu/kT} nh\nu}{\sum_{n=0}^{\infty} N_0 e^{-nh\nu/kT}}$$

Taking $x = e^{-h\nu/kT}$, this can be expanded as

$$\bar{\varepsilon} = h\nu x\left(\frac{1 + 2x + 3x^2 + 4x^3 + \cdots}{1 + x + x^2 + x^3 + \cdots}\right)$$

$$= h\nu x \frac{(1-x)^{-2}}{(1-x)^{-1}} = \frac{h\nu x}{1-x}$$

$$= \frac{h\nu}{e^{h\nu/kT} - 1}$$

Multiplying it by the Jeans' number (Equation 2.2) the energy density of the radiation inside the cavity becomes

$$\boxed{U(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}} \tag{2.7}$$

This is **Planck's radiation law**. In terms of the wavelength λ of the radiation, this becomes

$$\boxed{U(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}} \tag{2.8}$$

Planck's law agrees very closely with the observed spectral distribution curves for all values of λ and T. It reduces to Wien's law as $\lambda \to 0$ and Rayleigh-Jeans' law as $\lambda \to \infty$. Further, it is found to be consistent with Wien's displacement law, $\lambda_m T$ = constant, and Stefan's law, $U \propto T^4$. Thus, it incorporates all that is valid from the classical theory and yet, makes a fundamental departure, which ultimately shook the foundations of classical mechanics. Planck was awarded the 1918 Nobel Prize for the discovery of energy quanta.

PROBLEM 2.1 Show that Planck's law reduces to Wien's law in the short wavelength limit and Rayleigh-Jeans' law in the long wavelength limit.

Solution: When λ is small, $e^{hc/\lambda kT} >> 1$. Therefore,

$$U(\lambda, T) \sim \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT}$$

which is *Wien's law* (see Equation 2.1).

When λ is large,

$$e^{hc/\lambda kT} \sim 1 + \frac{hc}{\lambda kT}$$

Therefore,

$$U(\lambda, T) \sim \frac{8\pi hc}{\lambda^5} \frac{\lambda kT}{hc}$$

$$= \frac{8\pi kT}{\lambda^4}$$

which is *Rayleigh-Jeans' law* (Equation 2.4).

2.2 THE PHOTOELECTRIC EFFECT

When electromagnetic radiation of high enough frequency is incident on a metal surface, electrons are emitted from the surface. This phenomenon is called *photoelectric effect*. The emitted electrons are generally called *photoelectrons*. This effect was discovered by Heinrich Hertz in 1887.

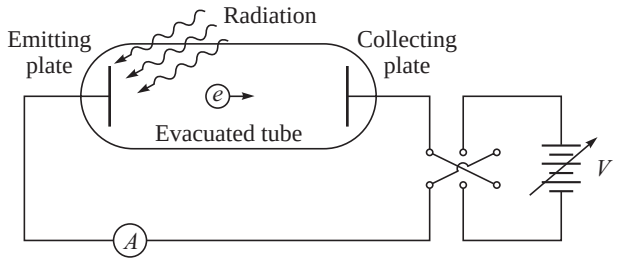

Figure 2.2 Apparatus for the study of photoelectric effect.

The apparatus used to study the photoelectric effect is shown in Figure 2.2. When the collecting plate is given sufficiently high positive potential V, all the emitted electrons reach the collecting plate and the photoelectric current saturates.

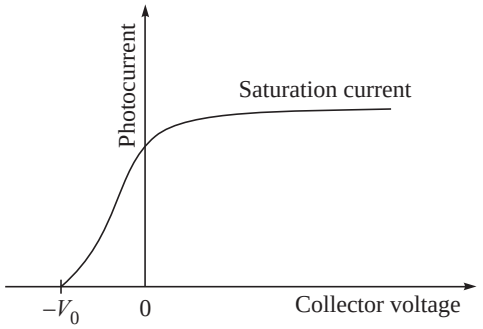

Figure 2.3 Photocurrent vs. collector voltage.

The following interesting results were obtained in the study:

(1) No electrons are emitted if the incident radiation has a frequency less than a *threshold* value ν_0. The value of ν_0 varies from metal to metal.
(2) The kinetic energy of the emitted electrons varies from zero to a maximum value. The maximum value of energy depends on the frequency and not on the intensity of radiation. It varies linearly with the frequency.
(3) The number of photoelectrons emitted per second, or the photoelectric current, is proportional to the intensity of radiation but is independent of the frequency.
(4) The photoelectric emission is an instantaneous process, *i.e.*, there is negligible time lag between the incidence of radiation and the emission of electrons, regardless of how low the intensity of radiation is.

Failure of Classical Physics

These results, except number three, cannot be explained if we consider radiation to be wave-like, obeying classical electromagnetic theory. Classically, the

maximum energy of the emitted electrons should increase with the intensity of incident radiation. The frequency of radiation has nothing to do with it. The reason is that the force exerted on the electrons in the metal should be proportional to the magnitude of the electric field $\boldsymbol{E}$ of the incident wave, and the magnitude of $\boldsymbol{E}$ increases when the intensity of the radiation is increased. Contrary to this, it is observed that the energy of the photoelectrons is independent of the intensity of light but depends on the frequency. Further, classically, electromagnetic energy is absorbed by the electron gradually and the electron can be ejected only when this energy becomes more than the *work function*† of the metal. Therefore, there may be a time lag between the onset of the radiation and the emission of the electron. The lag will be longer when the intensity of radiation is decreased. No such time lags have ever been observed, even with radiation of very low intensity. All observed time lags have been less than or equal to 10^{-9} seconds.

Einstein's Theory—Photons

Einstein explained the photoelectric effect using Planck's quantum hypothesis. In order to explain the spectral distribution of blackbody radiation, Planck had assumed that the exchange of energy between the walls of a cavity and the radiation of frequency ν takes place in quanta of magnitude $h\nu$, where h is called Planck's constant. Einstein went one step further. He suggested that *the incident radiation itself acts like a stream of tiny bundles or quanta of energy* $h\nu$. These quanta later came to be known as *photons*††. When a photon collides with an electron in the metal surface, it can be absorbed, imparting all its energy to the electron instantaneously. If the work function of the metal is W, then this much energy is expanded to remove the electron from the surface. Therefore, the maximum kinetic energy $E_{\max}$, and the corresponding velocity $v_{\max}$, of the emitted electron are given by

$$\boxed{E_{\max} = \frac{1}{2} m v_{\max}^2 = h\nu - W} \tag{2.9}$$

This is called *Einstein's photoelectric equation*. It shows that $E_{\max}$ varies linearly with the frequency ν of the incident radiation.

The *threshold frequency* ν_0 corresponds to the situation when all of the energy of the photon is used up to remove the electron from the metal and so no energy is left to provide its kinetic energy. Thus, ν_0 is given by

$$h\nu_0 = W$$

or

$$\boxed{\nu_0 = \frac{W}{h}} \tag{2.10}$$

† *Work function* of a material is the minimum amount of energy required to remove an electron from its surface.

†† Einstein did not introduce the name *photon*. It was coined much later, in 1926, by G.N. Lewis.

Substituting in (2.9), we obtain

$$\boxed{E_{\max} = h(\nu - \nu_0)} \tag{2.11}$$

as another version of the photoelectric equation. Clearly, no emission is possible if $\nu < \nu_0$.

An increase in the intensity of raditation results in an increase in the number of photons striking the metal per second but not in the energy of individual photons. Therefore, the number of photoelectrons emitted per second, and hence the photoelectric current, increases, but not the energy of photoelectrons.

Lastly, since the electron emission is the result of a direct collision between an electron and a photon, there is no time delay before emission starts.

Stopping Potential

If the collector plate in the photoelectric apparatus of Fig. 2.2 is made negative, the electrons are repelled back. For a certain value V_0 of this negative potential, the most energetic electrons are just turned back and therefore the photoelectric current becomes zero. This potential is called the *stopping* or *cut-off potential*. It is clear that

$$eV_0 = E_{\max}$$

Substituting in 2.11,

$$eV_0 = h(\nu - \nu_0)$$

or

$$\boxed{V_0 = \frac{h}{e}(\nu - \nu_0)} \tag{2.12}$$

This shows that $V_0 \propto \nu$.

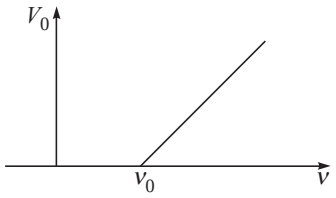

Figure 2.4

The variation of stopping potential with the frequency of the incident radiation is shown in Fig. 2.4. The graph is a straight line cutting the ν-axis at the threshold frequency ν_0. The slope of this graph is h/e. Thus, the value of Planck's constant can be determined by measuring the slope of this graph. This was done by Millikan who found that the value of h obtained from these graphs is the same as that obtained by Planck from the blackbody radiation experiments. This was a great achievement as it established the correctness of the quantum concept and Einstein's theory. Einstein was awarded the 1921 Nobel Prize and Millikan, the 1923 Nobel Prize.

PROBLEM 2.2 Find the number of photons emitted per second by a 40 W source of monochromatic light of wavelength 6000 Å.

Solution: Let the number of photons be n. Then

$$nh\nu = E$$

or
$$n = \frac{E}{h\nu} = \frac{E\lambda}{hc}$$

$$= \frac{40 \times 6000 \times 10^{-10}}{6.63 \times 10^{-34} \times 3 \times 10^{8}}$$

$$= \boxed{12.06 \times 10^{19}}$$

PROBLEM 2.3 The work function of a photosensitive surface is 3.2 eV. Will photoemission occur if a photon of energy 3.8 eV is incident on the surface? If yes, find in joules the maximum kinetic energy of the photoelectron.

Solution: Since the energy of the photon is more than the work function of the surface, photoemission will occur.

Kinetic energy of photoelectron

$$= 3.8 - 3.2 = 0.6 \text{ eV}$$
$$= 0.6 \times 1.6 \times 10^{-19} \text{ J}$$
$$= \boxed{9.6 \times 10^{-20} \text{ J}}$$

PROBLEM 2.4 The work function of a metal is 3.45 eV. What is the maximum wavelength of a photon that can eject an electron from the metal?

Solution: If ν_0 is the threshold frequency, then we have

$$h\nu_0 = W$$

or
$$\frac{hc}{\lambda_0} = W$$

Thus, maximum wavelength is

$$\lambda_0 = \frac{hc}{W} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{3.45 \times 1.6 \times 10^{-19}} = 3.603 \times 10^{-7} \text{ m}$$

$$= \boxed{3603 \text{ Å}}$$

PROBLEM 2.5 A metal of work function 3.0 eV is illuminated by light of wavelength 3000 Å. Calculate (a) the threshold frequency, (b) the maximum energy of photoelectrons, and (c) the stopping potential.

Solution:

(a) Threshold frequency

$$\nu_0 = \frac{W}{h} = \frac{3.0 \times 1.6 \times 10^{-19}}{6.63 \times 10^{-34}}$$

$$= \boxed{0.72 \times 10^{15} \text{ Hz}}$$

(b) Frequency of incident radiation

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{3 \times 10^{-7}} = 1 \times 10^{15} \text{ Hz}$$

Maximum energy of photoelectrons $E_{max} = h(\nu - \nu_0)$

$$= 6.63 \times 10^{-34} (1.0 - 0.72) \times 10^{15}$$

$$= 1.86 \times 10^{-19} \text{ J}$$

$$= \frac{1.86 \times 10^{-19}}{1.6 \times 10^{-19}} = \boxed{1.16 \text{ eV}}$$

(c) Stopping potential $V_0 = \frac{E_{max}}{e} = \frac{1.86 \times 10^{-19}}{1.6 \times 10^{-19}}$

$$= \boxed{1.16 \text{ V}}$$

PROBLEM 2.6 Find the frequency of the light which ejects from a metal surface electrons fully stopped by a retarding potential of 3 V. The photoelectric effect begins in this metal at a frequency of 6×10^{14} s^{-1}. Find the work function for this metal.

Solution:

Threshold frequency $\nu_0 = 6 \times 10^{14} \text{ s}^{-1}$

Work function $W = h\nu_0 = 6.63 \times 10^{-34} \times 6 \times 10^{14}$

$$= 39.78 \times 10^{-20} \text{ J}$$

$$= \frac{39.78 \times 10^{-20}}{1.6 \times 10^{-19}} = \boxed{2.486 \text{ eV}}$$

Now, $eV_0 = h\nu - h\nu_0$

Therefore, $\nu = \frac{eV_0 + h\nu_0}{h}$

$$= \frac{1.6 \times 10^{-19} \times 3 + 39.78 \times 10^{-20}}{6.63 \times 10^{-34}}$$

$$= \boxed{1.32 \times 10^{15} \text{ s}^{-1}}$$

PROBLEM 2.7 Work function of Na is 2.3 eV. Does sodium show photoelectric emission for light of wavelength 6800 Å? ($h = 6.6 \times 10^{-34}$ Js).

Solution: $\lambda = 6800 \text{ Å} = 6800 \times 10^{-10} \text{ m}$

Energy of incident photon $= \frac{hc}{\lambda}$

$$= \frac{6.6\times10^{-34}\times3\times10^{8}}{6800\times10^{-10}}\ \text{J}$$

$$= \frac{6.6\times3}{68}\times\frac{10^{-18}}{1.6\times10^{-19}}\ \text{eV}$$

$$= 1.83\ \text{eV}$$

Since the energy of incident photon is less than the work function of Na, *photoelectric emission is not possible with the given light.*

PROBLEM 2.8 Light of wavelength 3500 Å is incident on two metals *A* and *B*. Which metal will yield photoelectrons if their work functions are 4.2 eV and 1.9 eV, respectively.

Solution: $\lambda = 3500$ Å

Energy of incident photon $E = \dfrac{hc}{\lambda}$

$$= \frac{6.6\times10^{-34}\times3\times10^{8}}{3500\times10^{-10}\times1.6\times10^{-19}}\ \text{eV}$$

$$= 3.53\ \text{eV}$$

Since 1.9 eV < E < 4.2 eV, *only metal B will yield photoelectrons*.

PROBLEM 2.9 Calculate the maximum kinetic energy of a photoelectron (in eV) emitted on shining light of wavelength 6.2×10^{-6} m on a metal surface. The work function of the metal is 0.1 eV.

Solution: $\lambda = 6.2\times10^{-6}$ m, $W = 0.1$ eV

Maximum kinetic energy of a photoelectron is given by

$$E_{\max} = h\nu - W$$

$$= \frac{hc}{\lambda} - W$$

$$= \left[\frac{6.6\times10^{-34}\times3\times10^{8}}{6.2\times10^{-6}\times1.6\times10^{-19}} - 0.1\right]\text{eV}$$

$$= \left[\frac{66\times3}{62\times16} - 0.1\right] = 0.2 - 0.1 = \boxed{0.1\,\text{eV}}$$

PROBLEM 2.10 In an experiment on photoelectric effect, the slope of the cut-off voltage versus frequency of incident light graph is found to be 4.12×10^{-15} Vs. Given $e = 1.60\times10^{-19}$ C, estimate the value of Planck's constant.

Solution: $eV_0 = h\nu - W$

or $$V_0 = \frac{h}{e}\nu - \frac{W}{e}$$

Therefore, slope of the $V_0 - \nu$ curve $= \frac{h}{e}$

or $$h = \text{slope} \times e$$
$$= 4.12 \times 10^{-15} \times 1.60 \times 10^{-19}$$
$$= \boxed{6.59 \times 10^{-34}\ \text{Js}}$$

PROBLEM 2.11 What should be the frequency of incident radiation to eject electrons of maximum speed 10^6 m/s from potassium metal? Work function of potassium is 2.26 eV.

Solution: $W = 2.26\ \text{eV} = 2.26 \times 1.6 \times 10^{-19}\ \text{J}$
$= 3.61 \times 10^{-19}\ \text{J}$

Now,

$$\frac{1}{2}mv_{\max}^2 = h\nu - W$$

or $$h\nu = \frac{1}{2}mv_{\max}^2 + W$$
$$= \frac{1}{2} \times 9 \times 10^{-31} \times (10^6)^2 + 3.61 \times 10^{-19}$$
$$= 4.55 \times 10^{-19} + 3.61 \times 10^{-19} = 8.16 \times 10^{-19}$$

Therefore, $$\nu = \frac{8.16 \times 10^{-19}}{6.6 \times 10^{-34}} = \boxed{1.23 \times 10^{15}\ \text{Hz}}$$

PROBLEM 2.12 (a) A stopping potential of 0.82 V is required to stop the emission of photoelectrons from the surface of a metal by light of wavelength 4000 Å. For light of wavelength 3000 Å, the stopping potential is 1.85 V. Find the value of Planck's constant.

(b) At stopping potential, if the wavelength of the incident light is kept fixed at 4000 Å but the intensity of light is increased two times, will photoelectric current be obtained? Give reasons for your answer.

Solution: (a) We have $\frac{hc}{\lambda_1} = eV_1 + W$ and $\frac{hc}{\lambda_2} = eV_2 + W$. Subtraction gives

$$hc\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right) = e(V_2 - V_1)$$

or $$h = \frac{e(V_2 - V_1)}{c\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)}$$

$$= \frac{1.6\times10^{-19}(1.85-0.82)}{3\times10^{8}\left(\frac{1}{3\times10^{-7}}-\frac{1}{4\times10^{-7}}\right)}$$

$$= \boxed{6.592\times10^{-34}\ \text{Js}}$$

(b) *No*, because the stopping potential depends only on the wavelength of light and not on its intensity.

PROBLEM 2.13 Light of wavelength 4560 Å and power 1 mW is incident on a caesium surface. Calculate the photoelectric current, assuming a quantum efficiency of 0.5%. Work function of cesium = 1.93 eV; $h = 6.62 \times 10^{-34}$ Js.

Solution: Energy of one photon = $h\nu = \frac{hc}{\lambda}$

$$= \frac{6.62\times10^{-34}\times3\times10^{8}}{4560\times10^{-10}} = 4.32 \times 10^{-19}\ \text{J}$$

Number of photons incident on the surface per second

$$= \frac{1\times10^{-3}}{4.32\times10^{-19}} = 2.32 \times 10^{15}$$

Only 0.5% of the incident photons release electrons. Therefore, the number of electrons released per second is

$$n = 2.32 \times 10^{15} \times \frac{0.5}{100} = 1.16 \times 10^{13}$$

The photoelectric current

$$= ne$$
$$= 1.16 \times 10^{13} \times 1.6 \times 10^{-19}$$
$$= \boxed{1.86\times10^{-6}\ \text{A}}$$

2.3 THE COMPTON EFFECT

When a monochromatic beam of X-rays is scattered by an element of low atomic weight (for example carbon), it is observed that the scattered X-rays, at all angles, have maximum intensities at two wavelengths, one at the original wavelength and the other at a slightly longer wavelength. The wavelength shift is independent of the wavelength of the incident beam and the scattering material; it depends only on the scattering angle. This phenomenon is called the *Compton effect*. It was discovered by A.H. Compton in 1923, who also gave an explanation of it in terms of quantum theory.

Compton effect provides the most direct evidence for the particle nature of radiation. Compton was awarded the 1927 Nobel Prize for the discovery and explanation of this effect.

Experimental Arrangement

Figure 2.5 shows a schematic diagram of an experimental arrangement for observing Compton scattering. A monochromatic beam of X-rays of known wavelength is directed at a block of some scattering material, say graphite. The scattered X-rays are received by a Bragg X-ray spectrometer to measure their wavelength and intensity. The spectrometer can rotate about the scattering target so that measurements can be made at different angles.

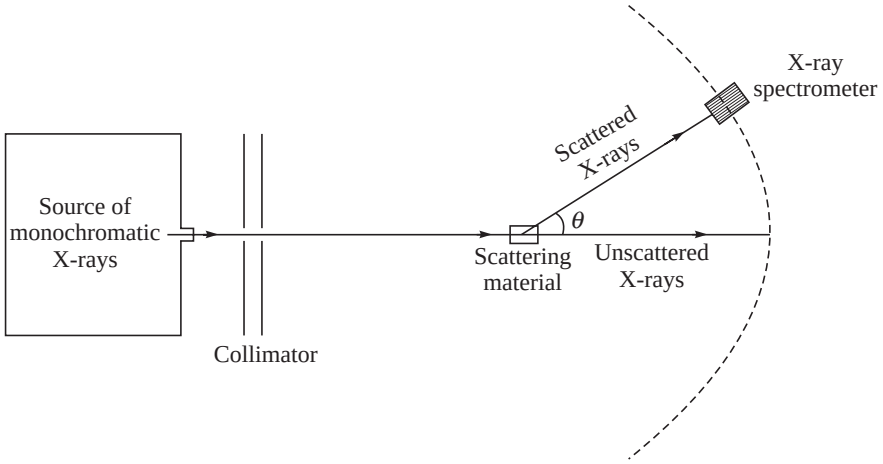

Figure 2.5 Experimental arrangement for observing Compton scattering.

The results obtained by Compton for $\theta = 0°$, 45°, 90° and 135° are shown in Figure 2.6. It may be noted that at each non-zero angle, the scattered beam consists of two peaks– one corresponding to the original wavelength (λ_0) and the other due to the *modified* wavelength (λ). The *wavelength shift* $\Delta\lambda$ increases with the increase of scattering angle θ.

Failure of Classical Physics

Let us try to understand this phenomenon on the basis of classical electromagnetic theory. The X-ray beam, on entering the scattering material, interacts with the atomic electrons. The "outer" electrons can be considered essentially free because they are bound to the atoms with an energy which is much smaller than the energy of the X-ray beam. The electric field associated with the X-ray exerts a force on these electrons and makes them oscillate simple harmonically with the frequency of the X-ray. The electrons, being accelerated, will emit electromagnetic radiation. The initial frequency of this radiation will be equal to that of the incident X-ray.

The X-ray beam also imparts some momentum to the electron, which then recoils in the direction of propagation of the beam. As the electron moves away from the source of the X-ray, it "sees" a lower frequency due to Doppler effect.

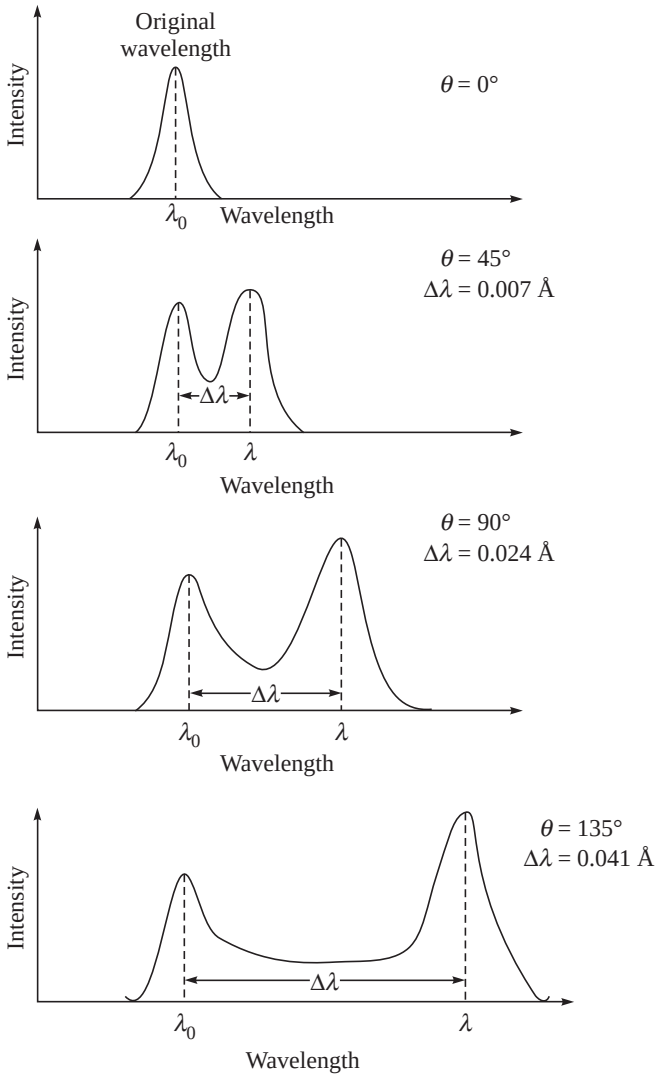

Figure 2.6 Variation of the shifted line with scattering angle. The peak at λ_0 is due to the incident beam.

The electron then emits radiation of this lower frequency. The frequency will decrease continuously till the electron has attained its final speed after scattering the entire beam. Thus, classically, the wavelengths of scattered X-rays should have a continuous range of values, which is contrary to experimental observation.

Compton's Explantation

Compton was able to explain this phenomenon using the quantum theory of radiation, developed by Planck and Einstein. He considered the incident X-rays

as a stream of *photons*, each of energy $h\nu$ and momentum $h\nu/c$, where ν is the frequency of radiation, h is the Planck's constant and c is the speed of light. The scattering process is treated as an elastic collision between a photon and a "free" electron, which is initially at rest (Figure 2.7). In the collision, a part of the photon energy is transferred to the electron which recoils. Therefore, the scattered photon has a smaller energy and hence a lower frequency (higher wavelength).

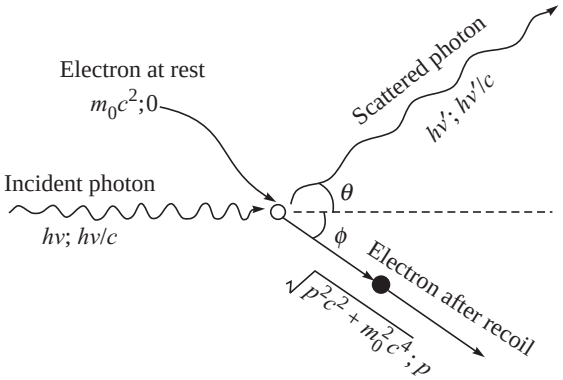

Figure 2.7 Collision of a photon with an electron initially at rest.

Let ν' be the frequency of the scattered photon, m_0 be the rest mass of the electron and p be the recoil momentum of the electron. According to the theory of relativity, the energy of the electron at rest is m_0c^2 and that after recoil is $(p^2c^2 + m_0^2c^4)^{1/2}$. From the law of conservation of energy,

$$h\nu' + (p^2c^2 + m_0^2c^4)^{1/2} = h\nu + m_0c^2$$

or $$p^2c^2 + m_0^2c^4 = [h(\nu - \nu') + m_0c^2]^2$$

or $$p^2c^2 + m_0^2c^4 = h^2(\nu - \nu')^2 + 2h(\nu - \nu')m_0c^2 + m_0^2c^4$$

or $$\frac{p^2c^2}{h^2} = (\nu - \nu')^2 + \frac{2m_0c^2}{h}(\nu - \nu') \qquad (2.13)$$

Applying the law of conservation of momentum along and perpendicular to the direction of the incident photon,

$$p\cos\phi + \frac{h\nu'}{c}\cos\theta = \frac{h\nu}{c}$$

and $$p\sin\phi = \frac{h\nu'}{c}\sin\theta$$

Rearranging these equations,

$$\frac{pc}{h}\cos\phi = \nu - \nu'\cos\theta \qquad (2.14)$$

and $$\frac{pc}{h}\sin\phi = \nu'\sin\theta \qquad (2.15)$$

Squaring and adding (2.14) and (2.15),

$$\frac{p^2c^2}{h^2} = (\nu - \nu'\cos\theta)^2 + \nu'^2\sin^2\theta$$
$$= \nu^2 - 2\nu\nu'\cos\theta + \nu'^2$$
$$= (\nu - \nu')^2 + 2\nu\nu' - 2\nu\nu'\cos\theta$$
$$= (\nu - \nu')^2 + 2\nu\nu'(1 - \cos\theta) \qquad (2.16)$$

Comparing (2.13) and (2.16), we get

$$\frac{2m_0c^2}{h}(\nu - \nu') = 2\nu\nu'(1 - \cos\theta)$$

or
$$\frac{\nu - \nu'}{\nu\nu'} = \frac{h}{m_0c^2}(1 - \cos\theta)$$

or
$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_0c^2}(1 - \cos\theta) \qquad (2.17)$$

If λ and λ' are the wavelengths of the incident and scattered photons, then

$$\nu' = \frac{c}{\lambda'} \quad \text{and} \quad \nu = \frac{c}{\lambda}$$

Therefore, (2.17) can be expressed as

$$\boxed{\lambda' - \lambda = \Delta\lambda = \frac{h}{m_0c}(1 - \cos\theta)} \qquad (2.18)$$

or, equivalently,

$$\boxed{\Delta\lambda = \frac{2h}{m_0c}\sin^2\frac{\theta}{2}} \qquad (2.19)$$

The above equation shows that the **Compton shift** in wavelength is independent of the wavelength (or energy) of the incident photon and depends only on the angle of scattering–it increases with the angle. The quantity h/m_0c is called the *Compton wavelength of the electron.* Its value is 0.0242 Å. The name is rather misleading. This quantity is *not* the wavelength of the electron; it is the shift in the wavelength of a photon scattered off an electron at 90° to the initial direction.

The presence of the "unmodified" peak at each angle was explained by Compton as being due to the scattering of a photon by the atom as a whole. If m_0 is replaced by the mass of the atom, the change in the wavelength is negligible because an atom is many thousands time more heavy than an electron.

Relation between θ and ϕ

Dividing (2.14) by (2.15),

$$\cot\phi = \frac{\nu - \nu'\cos\theta}{\nu'\sin\theta}$$

$$= \frac{1}{\sin\theta}\left(\frac{\nu}{\nu'} - \cos\theta\right) \tag{2.20}$$

From (2.17),

$$\frac{\nu}{\nu'} = 1 + \alpha(1 - \cos\theta) \tag{2.21}$$

where $\alpha = h\nu/m_0c^2$. Substituting in (2.20),

$$\cot\phi = \frac{1}{\sin\theta}[1 + \alpha(1 - \cos\theta) - \cos\theta]$$

$$= \frac{(1+\alpha)(1-\cos\theta)}{\sin\theta}$$

$$= \frac{(1+\alpha)\left(2\sin^2\frac{\theta}{2}\right)}{2\sin\frac{\theta}{2}\cos\frac{\theta}{2}}$$

or $$\boxed{\cot\phi = (1+\alpha)\tan\frac{\theta}{2}} \tag{2.22}$$

This is the required relation.

Kinetic Energy of the Recoil Electron

The kinetic energy of the recoil electron is

$$E = h\nu - h\nu'$$

From (2.21),

$$\nu' = \frac{\nu}{1+\alpha(1-\cos\theta)}$$

Therefore,

$$E = h\nu\left[1 - \frac{1}{1+\alpha(1-\cos\theta)}\right]$$

or $$\boxed{E = h\nu\,\frac{\alpha(1-\cos\theta)}{1+\alpha(1-\cos\theta)}} \tag{2.23}$$

The kinetic energy can also be expressed in terms of angle ϕ. Let us rewrite (2.23) as

$$E = h\nu\,\frac{\alpha\left(2\sin^2\frac{\theta}{2}\right)}{1+\alpha\left(2\sin^2\frac{\theta}{2}\right)}$$

$$= h\nu \frac{2\alpha}{\text{cosec}^2 \frac{\theta}{2} + 2\alpha} \tag{2.24}$$

Now, from (2.22),

$$\cot\frac{\theta}{2} = (1 + \alpha)\tan\phi$$

or $$\cot^2\frac{\theta}{2} = (1 + \alpha)^2\tan^2\phi$$

or $$\text{cosec}^2\frac{\theta}{2} - 1 = (1 + \alpha)^2(\sec^2\phi - 1)$$

$$= (1 + \alpha)^2 \sec^2\phi - (1 + \alpha)^2$$

$$= (1 + \alpha)^2 \sec^2\phi - 1 - 2\alpha - \alpha^2$$

or $$\text{cosec}^2\frac{\theta}{2} + 2\alpha = (1 + \alpha)^2 \sec^2\phi - \alpha^2$$

Substituting this in (2.24),

$$E = h\nu \frac{2\alpha}{(1+\alpha)^2 \sec^2\phi - \alpha^2}$$

or $$\boxed{E = h\nu \frac{2\alpha \cos^2\phi}{(1+\alpha)^2 - \alpha^2\cos^2\phi}} \tag{2.25}$$

The correctness of (2.22) and (2.23) (or 2.25) have been verified experimentally with great care several times. It has also been shown that the recoil of the electron occurs simultaneously with the scattering of the photon. Thus Compton's theory has been thoroughly tested. Compton's work established the existence of photons as real particles having momentum as well as energy.

PROBLEM 2.14 X-rays of wavelength 2.0 Å are scattered from a carbon block. The scattered photons are observed at right angles to the direction of the incident beam.

Calculate (a) the wavelength of the scattered photon, (b) the energy of the recoil electron, and (c) the angle at which the recoil electron appears.

Given: Rest mass of an electron $m_0 = 9.1 \times 10^{-31}$ kg, $c = 3 \times 10^8$ m/s, $h = 6.6 \times 10^{-34}$ Js.

Solution: (a) If λ and λ' are the wavelengths of the incident and the scattered photons, respectively, and θ is the scattering angle, then

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0 c}(1 - \cos\theta)$$

$$= \frac{6.6\times10^{-34}}{9.1\times10^{-31}\times3\times10^8}(1 - \cos 90°)$$

$$= 2.4 \times 10^{-12} \text{ m}$$

$$= 0.024 \text{ Å}$$

Therefore, $\lambda' = \lambda + \Delta\lambda = \boxed{2.024\ \text{Å}}$

(b) Neglecting the binding energy of the electron, its recoil energy is given by

$$E = h(\nu - \nu')$$
$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)$$
$$= \frac{hc(\lambda' - \lambda)}{\lambda\lambda'}$$
$$= \frac{6.6\times10^{-34}\times3\times10^{8}\times0.024\times10^{-10}}{2.0\times10^{-10}\times2.024\times10^{-10}}$$
$$= \boxed{1.17\times10^{-17}\ \text{J}}$$

(c) The angle ϕ at which the recoil electron appears is given by

$$\cot\phi = \frac{1}{\sin\theta}\left(\frac{\nu}{\nu'} - \cos\theta\right)$$
$$= \frac{1}{\sin\theta}\left(\frac{\lambda'}{\lambda} - \cos\theta\right)$$
$$= \frac{1}{\sin90°}\left(\frac{2.024}{2.0} - \cos90°\right)$$
$$= 1.012$$

or $\phi = \cot^{-1}(1.012)$

$$= \boxed{44°40'}$$

PROBLEM 2.15 A photon of energy 0.9 MeV is scattered through 120° by a free electron. Calculate the energy of the scattered photon.

Solution: From (2.21),

$$\nu' = \frac{\nu}{1 + \frac{h\nu}{m_0c^2}(1 - \cos\theta)}$$

Energy of the scattered photon

$$h\nu' = \frac{h\nu}{1 + \frac{h\nu}{m_0c^2}(1 - \cos\theta)}$$
$$= \frac{h\nu}{1 + \frac{2h\nu}{m_0c^2}\sin^2\frac{\theta}{2}}$$

Here $h\nu = 0.9$ MeV,

$$\theta = 120°,$$
$$m_0c^2 = 0.51 \text{ MeV}$$

Therefore,

$$h\nu' = \frac{0.9}{1 + 2 \times \frac{0.9}{0.51}\left(\frac{3}{4}\right)}$$
$$= \boxed{0.247 \text{ MeV}}$$

PROBLEM 2.16 In a Compton scattering experiment, the incident radiation has wavelength 2.000 Å while the wavelength of the radiation scattered through 180° is 2.048 Å. Calculate (a) the wavelength of the radiation scattered at an angle of 60° to the direction of incidence, and (b) the energy of the recoil electron which scatters the radiation through 60°.

Solution: We have

$$\lambda' - \lambda = \frac{h}{m_0c}(1 - \cos\theta)$$

When $\theta = 180°$, this gives

$$(2.048 - 2.000) \times 10^{-10} = \frac{h}{m_0c}(1 - \cos 180°)$$

or
$$\frac{h}{m_0c} = \frac{0.048 \times 10^{-10}}{2} = 0.024 \times 10^{-10} \text{ m}$$

(a) When $\theta = 60°$,

$$\lambda' = 2.000 \times 10^{-10} + 0.024 \times 10^{-10}[1 - \cos 60°]$$
$$= 2.012 \times 10^{-10} \text{ m} = \boxed{2.012 \text{ Å}}$$

(b) Energy of the recoil electron

$$= h\nu - h\nu'$$
$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right) = \frac{hc(\lambda' - \lambda)}{\lambda\lambda'}$$
$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8 (2.012 - 2.000) \times 10^{-10}}{2.000 \times 10^{-10} \times 2.012 \times 10^{-10}}$$
$$= \boxed{5.91 \times 10^{-18} \text{ J}}$$

PROBLEM 2.17 In a Compton scattering experiment, the X-ray photon is scattered at an angle of 180° and the electron recoils with an energy of 4 keV. Calculate the wavelength of the incident photon.

Solution: Kinetic energy of the recoil electron

$$E = 4 \times 10^3 \times 1.6 \times 10^{-19}$$

$$= 6.4 \times 10^{-16} \text{ J}$$

Momentum of the electron

$$p = \sqrt{2m_0E}$$
$$= \sqrt{2 \times 9.1 \times 10^{-31} \times 6.4 \times 10^{-16}}$$
$$= 34.13 \times 10^{-24} \text{ kg m/s}$$

Let λ be the wavelength of the incident photon and λ' that of the scattered photon. Then conservation of energy gives

$$\frac{hc}{\lambda} - \frac{hc}{\lambda'} = 6.4 \times 10^{-16} \quad \text{(i)}$$

It is given that $\theta = 180°$. Therefore, using (2.22), we get $\phi = 0°$. Thus, the electron recoils in the direction of the incident photon. Applying the law of conservation of momentum in the direction of the incident photon,

$$\frac{h}{\lambda} = \frac{h}{\lambda'} \cos 180° + p \cos 0°$$

or
$$\frac{h}{\lambda} + \frac{h}{\lambda'} = 34.13 \times 10^{-24}$$

Multiplying both sides by c,

$$\frac{hc}{\lambda} + \frac{hc}{\lambda'} = 34.13 \times 10^{-24} \times 3 \times 10^8 = 102.39 \times 10^{-16} \quad \text{(ii)}$$

Adding (i) and (ii),

$$\frac{2hc}{\lambda} = 108.79 \times 10^{-16}$$

or
$$\lambda = \frac{2 \times 6.3 \times 10^{-34} \times 3 \times 10^8}{108.79 \times 10^{-16}}$$
$$= 0.347 \times 10^{-10} \text{ m}$$
$$= \boxed{0.35 \text{ Å}}$$

PROBLEM 2.18 (a) What is the maximum kinetic energy that can be imparted to a free electron by a photon of initial frequency ν? (b) Is it possible for the photon to transfer all of its energy to the electron?

Solution: (a) The kinetic energy of the recoil electron is (Equation 2.23)

$$E = h\nu \frac{\alpha(1 - \cos\theta)}{1 + \alpha(1 - \cos\theta)}$$

The maximum value of E corresponds to maximum Compton shift, which, according to (2.18), happens when $\theta = 180°$. Thus,

$$E_{\max} = h\nu \frac{\alpha(1 - \cos 180°)}{1 + \alpha(1 - \cos 180°)}$$

$$= \boxed{h\nu\left(\frac{2\alpha}{1+2\alpha}\right)}$$

(b) From the above expression it is obvious that

$$E_{max} < h\nu$$

Thus, a photon *cannot* transfer all of its energy to a free electron.

PROBLEM 2.19 Gamma ray photons of energy 1.02 MeV are scattered from electrons which are initially at rest. (a) Find the angle for symmetric scattering (i.e., $\theta = \phi$) at this energy. (b) What is the energy of the scattered photons for this case?

Solution: (a) We have

$$\cot\phi = (1 + \alpha)\tan\frac{\theta}{2}$$

Putting $\phi = \theta$,

$$\frac{\cos\theta}{\sin\theta} = (1 + \alpha)\frac{\sin(\theta/2)}{\cos(\theta/2)}$$

or $$\cos\theta = 2(1 + \alpha)\sin^2(\theta/2)$$

or $$1 - 2\sin^2(\theta/2) = 2(1 + \alpha)\sin^2(\theta/2)$$

or $$\sin\frac{\theta}{2} = \frac{1}{\sqrt{2(\alpha+2)}}$$

$$= \frac{1}{\sqrt{2\left(\frac{1.02}{0.51}+2\right)}} = \frac{1}{\sqrt{8}}$$

or $$\theta = 2\sin^{-1}\left(\frac{1}{\sqrt{8}}\right) = \boxed{41.4°}$$

(b) Energy of the scattered photon is

$$h\nu' = \frac{h\nu}{1+\alpha(1-\cos\theta)}$$

$$= \frac{1.02}{1+2(1-\cos 41.4°)}$$

$$= \frac{1.02}{1+2(1-0.750)}$$

$$= \boxed{0.68 \text{ MeV}}$$

2.4 DUAL NATURE OF RADIATION

In order to explain several phenomena like interference, diffraction and polarization, it is necessary to assume that electromagnetic radiation has wave

nature. The wave theory of radiation was firmly established by the end of the nineteenth century. Maxwell provided the theoretical framework for it.

On the other hand, as we have discussed above, to explain the observed results connected with the interaction of radiation with matter, such as the blackbody radiation, the photoelectric effect and the Compton effect, it becomes necessary to assume that radiation has particle nature—it is emitted or absorbed in the form of discrete quanta called photons. Thus, we have to accept the paradoxical situation that radiation has dual nature. However, it does not exhibit both characteristics in a single experiment. In a given experiment it behaves either as a particle or as a wave. The wave and particle aspects of radiation *complement* each other.

As we shall see later, this dual characterter is not confined to radiation alone but is exhibited by material particles as well.

Conceptual Difficulty

This dual behaviour of radiation—and also of material particles as we shall see later—raises a serious conceptual difficulty. We shall discuss this in the context of the famous Young's double-slit experiment. Light from a source is passed through two close, narrow slits and an interference pattern is observed on a screen. We know that this pattern is completely explained by classical wave theory. The pattern does not depend on the intensity of the beam. Now, we have just seen that light consists of photons. At first, we might be naturally tempted to assume that the interference takes place between different photons passing through the two slits. Now, suppose the intensity of the beam is gradually decreased until only one photon is released from the source at a time. It is found that the interference pattern still appears, though after a sufficiently long time. If one of the slits is closed, the pattern disappears. This is strange. How is it that a stream of photons, coming one at a time, each of which can go through only one of the two slits, produces an interference pattern only when both the slits are open. The only possible explanation is that each photon "knows" that there are two slits and it *interferes with itself*!

Can we say that a photon splits itself into pieces? No, because all the experimental evidences (e.g. Compton effect) are against this possibility. We are forced to accept that classical physics cannot explain this phenomenon. The search for an explanation of such conflicting and puzzling situations led to the development of quantum mechanics, which is able to describe them well.

SUMMARY

1. Classical physics failed to explain the spectral distribution of radiant energy emitted by a blackbody.
2. In order to explain this distribution, Planck proposed the *quantum hypothesis* according to which a material oscillator of frequency ν can

emit or absorb electromagnetic energy, not continuously in arbitrarily small amounts, but in multiples of the quantum $h\nu$. The constant h, called Planck's constant, has the value 6.625×10^{-34} Js. The energy density of the radiation inside the enclosure which acts as a blackbody at temperature T, is

$$U(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

3. Einstein extended Planck's idea to explain the photoelectric effect. He assumed that the incident radiation acts like a stream of tiny bundles or quanta of energy $h\nu$. These quanta, called *photons*, behave like particles. When a photon collides with an electron in the metal, the electron is emitted with maximum energy given by

$$E_{\max} = h(\nu - \nu_0)$$

where ν_0 is called the threshold frequency, which is related to the work function W of the metal as

$$\nu_0 = \frac{W}{h}$$

4. Compton explained the shift in the wavelength of X-rays scattered by free electrons by considering the scattering process as an elastic collision between a photon and a free electron. Photons were considered to have energy $h\nu$ and momentum $h\nu/c$. Compton effect provides the most direct evidence for the particle nature of radiation.

If a photon is scattered by an angle θ, then the wavelength shift is given by

$$\Delta\lambda = \frac{2h}{m_0 c} \sin^2 \frac{\theta}{2}$$

where m_0 is the rest mass of the electron.

5. It is now accepted that radiation has dual nature. In some situations it behaves as a wave and in certain other situations it behaves as a particle. The wave and particle aspects of radiation are complementary.

The wave-particle duality raises conceptual difficulty in explaining certain phenomena, e.g., Young's double-slit interference. The explanation comes from modern quantum mechanics.

QUESTIONS

1. Discuss how classical approaches failed to account for the spectral distribution of energy density in the blackbody radiation. How did Planck overcome the difficulty? Derive Planck's radiation law.

2. (a) What is photoelectric effect? Draw a labelled diagram of the apparatus used to demonstrate it.

(b) What are the main features of photoelectric effect?
(c) Derive Einstein's photoelectric equation and explain how Einstein's theory accounts for the main features.

3. List the essential findings of the photoelectric experiments. How did Einstein explain the phenomenon? Why did Einstein's explanation seem so incredulous at that time, that Millikan experimented for ten years to disprove the findings?

4. Explain stopping potential and threshold frequency in photoelectric emission. Give an appropriate graph showing the variation of the stopping potential with the frequency of incident radiation. Explain how the value of Planck's constant can be determined using this graph.

5. (a) What is Compton effect? Give a schematic sketch of an experimental arrangement for observing this effect.
(b) Discuss why this effect cannot be explained on the basis of classical electromagnetic theory.
(c) What assumption did Compton make to explain this effect?

6. Obtain an expression for the change in wavelength of a photon when it is Compton scattered by a free electron through an angle θ with respect to the original direction.

7. Derive a relation between the angle of scattering of the photon and that of the electron in Compton effect.

8. A photon of frequency ν is scattered from a free electron at rest through an angle θ. Show that the ratio of the kinetic energy of the recoil electron to the energy of the incident photon is equal to

$$\frac{\alpha(1-\cos\theta)}{1+\alpha(1-\cos\theta)}$$

where $\alpha = h\nu/m_0c^2$, m_0 being the rest mass of the electron.

EXERCISES

1. Calculate the threshold frequency of photons for photoelectric emission from a metal of work function 0.05 eV. ($h = 6.6 \times 10^{-34}$ Js).

[***Ans.*** 1.2×10^{12} Hz]

2. The work function of a photosensitive material is 2.5 eV. What must be the threshold wavelength of incident light to eject electrons from it?

[***Ans.*** 5.0×10^{-7} m]

3. Light of wavelength 5000 Å falls on a metal surface of work function 1.9 eV. Find (a) the energy of a photon in eV, (b) the maximum kinetic energy of photoelectrons, and (c) the stopping potential.

[***Ans.*** (a) 2.5 eV, (b) 0.58 eV, (c) 0.58 V]

4. In an experiment, tungsten cathode, which has a photoelectric threshold wavelength of 2300 Å, is irradiated by ultraviolet light of wavelength

1800 Å. Calculate (a) the maximum energy of photoelectrons, and (b) the work function of tungsten. [***Ans.*** (a) 1.485 eV, (b) 5.38 eV]

5. Is it possible to liberate electrons from a metal surface, having work function 4.8 eV, with an incident radiation of wavelength (a) 2000 Å, (b) 5000 Å. [***Ans.*** (a) yes, (b) no]

6. A metal surface, when illuminated by light of frequency 0.90×10^{15} Hz, emits electrons which can be stopped by a retarding potential of 0.60 V. When the same surface is illuminated by light of frequency 1.26×10^{15} Hz, the required retarding potential is 2.1 V. Using these data calculate the value of Planck's constant and the work function of the metal.

[***Ans.*** 6.67×10^{-34} Js, 3.15 eV]

7. The photoelectric threshold wavelength for a metal is 3000 Å. Find the maximum kinetic energy of an electron ejected from it by radiation of wavelength 1200 Å. [***Ans.*** 6.2 eV]

8. The photoelectric threshold wavelength of sodium is 5420 Å. Calculate the maximum velocity of photoelectrons ejected by photons of wavelength 4000 Å. [***Ans.*** 5.36×10^5 m/s]

9. A retarding potential of 5 V just stops the fastest photoelectrons emitted from cesium. Calculate the wavelength of the most energetic incident photons? The work function of cesium is 1.8 eV. [***Ans.*** 1840 Å]

10. A photon of energy 1.02 MeV is scattered through 90° by a free electron. Calculate the energies of the photon and the electron after interaction.

[***Ans.*** 0.34 MeV, 0.68 MeV]

11. In a Compton scattering experiment, an incoming X-ray wavelength $\lambda = 5.53 \times 10^{-2}$ nm is scattered and detected at an angle of 35°. Find the fractional change in the wavelength of the scattered X-ray. Does the wavelength increase or decrease? [***Ans.*** 7.9×10^{-3}, increase]

12. X-rays of wavelength 1.82 Å are scattered from a thin aluminium foil. Scattered X-rays are observed at an angle of 60° from the incident beam. Calculate the wavelength of the scattered X-rays and the kinetic energy of the recoil electron. [***Ans.*** 1.832 Å, 7.15×10^{-18} J]

13. An X-ray photon is found to have doubled its wavelength on being Compton scattered by 90°. Find the wavelength and energy of the incident photon. [***Ans.*** 0.0242 Å, 0.51 MeV]

14. An X-ray photon of wavelength 1.0 Å is scattered at such an angle that the recoil electron has maximum kinetic energy. Calculate the wavelength of the scattered photon and the energy of the recoil electron.

[***Ans.*** 1.0486 Å, 575 eV]

15. For what wavelength of photon does Compton scattering result in a photon whose energy is one-half that of the original photon at a scattering angle of 45°. In which region of the electromagnetic spectrum does such a photon lie? (Compton wavelength of electron = 0.0242 Å).

[***Ans.*** 7.085×10^{-3} Å, γ-rays]

[**Hint.** $$h\nu' = \frac{h\nu}{1+\alpha\,(1-\cos\theta)}$$

$$\Rightarrow \qquad \frac{1}{2} = \frac{1}{1+\alpha(1-1/\sqrt{2})}$$

$$\Rightarrow \qquad \alpha = \frac{\sqrt{2}}{\sqrt{2}-1}$$

or $$\frac{h\nu}{m_0c^2} = \frac{\sqrt{2}}{\sqrt{2}-1}$$

or $$\left(\frac{h}{m_0c}\right)\left(\frac{1}{\lambda}\right) = \frac{\sqrt{2}}{\sqrt{2}-1}$$

or $$\lambda = (0.0242)\left(\frac{0.414}{1.414}\right)$$

$$= 7.085 \times 10^{-3}\ \text{Å}]$$

16. In a Compton experiment, at what scattering angle will incident 100 keV X-rays leave the target with an energy of 90 keV? [***Ans.*** 63.6°]

[**Hint.** $$1 + \alpha(1 - \cos\theta) = \frac{h\nu}{h\nu'} = \frac{100}{90}$$

or $$\alpha(1 - \cos\theta) = \frac{1}{9}$$

or $$1 - \cos\theta = \frac{1}{9\alpha} = \frac{1}{9}\frac{m_0c^2}{h\nu}$$

$$= \frac{1}{9}\left(\frac{0.51}{100\times10^{-3}}\right)$$

$$\Rightarrow \qquad \theta = \cos^{-1}(4/9)]$$

17. X-rays of wavelength 0.2400 nm are Compton scattered and the scattered beam is observed at an angle of 60° relative to the incident beam. Find (a) the wavelength of the scattered X-rays and (b) the direction of the scattered electrons.

[***Ans.*** (a) 0.2412 nm, (b) 60° relative to the incident beam]

18. What is the maximum percentage change in the wavelength of a 2.00 Å photon scattered by an electron? [***Ans.*** 2.42%]

19. Photons of energy 0.1 MeV undergo Compton scattering. Find the energy of a photon scattered at 60°, the recoil angle of the electron and the recoil kinetic energy of the electron.

[***Ans.*** 0.091 MeV, 55.4°, 0.009 MeV]

Chapter

3 Atoms and the Bohr Model

Chapter Contents

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3.1 INTRODUCTION

The concept of the atom was introduced by John Dalton in 1803 to explain the chemical combination of elements to form compounds. The idea got further confirmation when kinetic theory was developed to explain the behaviour of gases. However, real understanding of the structure of the atom became possible after the discovery of the electron by J.J. Thomson in 1897 and the realization that all atoms contain electrons. The electron is a negatively-charged particle having mass which is very small compared to the mass of an atom. Therefore, the atom must also contain positively-charged matter, having mass almost equal to the mass of the whole atom. Thomson suggested the *plum-pudding model* of the atom, according to which the electrons are embedded in a uniform sphere of positively-charged matter so that the atom as a whole is neutral.

Alpha-Scattering Experiment

In order to test the Thomson model, Geiger and Marsden carried out the following experiment in 1908 under the guidance of Rutherford. Alpha-particles from a

radioactive source were collimated into a narrow beam and then allowed to fall on thin metal foils. The α-particles scattered in different directions were detected. It was found that (a) most of the α-particles passed through the gold foil without appreciable deflection, and (b) some of the α-particles suffered fairly large deflections—in fact an unexpectedly large number even retraced their path.

The Rutherford Nuclear Model

It is obvious that the above results cannot be explained on the basis of Thomson's model. Observation (a) requires that most of the space in the metal foil must be empty. Observation (b) requires that the positively-charged matter in an atom cannot be uniformly distributed but must be concentrated in a small volume. Based on these facts, Rutherford proposed a new model known as the *nuclear model* or the *planetary model*. According to this model, the whole of the positive charge, which carries almost the entire mass of the atom, is concentrated in a tiny central core called the *nucleus*. The electrons revolve around the nucleus in orbits, leaving most of the volume of the atom unoccupied.

Difficulties with the Rutherford Model

The nuclear atom proposed by Rutherford could not be accepted due to the following problems. An electron moving in a circle is continuously accelerated towards the nucleus. According to classical electromagnetic theory, an accelerated charge radiates electromagnetic energy. As such, the energy of the electron would continuously decrease, its orbit would become smaller and smaller and ultimately it would spiral into the nucleus. However, we know that this does not happen and atoms are stable. Further, according to the classical theory, the frequency of the radiation emitted by the electron is equal to the frequency of revolution. Therefore, the spiralling electron would emit radiation of continuously increasing frequency till it falls into the nucleus. However, atoms do not radiate unless excited, in which case they radiate discrete, rather than continuous, frequencies. We discuss this in more detail below.

3.2 ATOMIC SPECTRA

All elements in atomic state emit line spectra. A line spectrum consists of narrow bright lines separated by dark intervals. It is characteristic of the atoms of the element which emits it. This makes spectroscopy a very important tool of chemical analysis because measurement of the wavelengths emitted by a material allows us to identify the elements present in it, even in very small amounts.

Experimental spectroscopy developed rapidly during the latter half of the nineteenth century. On studying the spectra carefully, it was found that the wavelengths present in the atomic spectrum of an element fall into sets which exhibit some definite pattern. Such a set is called a *spectral series*. The

wavelengths in each series can be expressed by an empirical formula and the formulae for the various series of an element are very similar. Hydrogen, being the simplest of all elements, was the first to be studied in detail.

In 1885, Johann Balmer showed that the wavelengths of all the spectral lines of the hydrogen atom known till then could be expressed by the formula

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, \ldots \tag{3.1}$$

The constant R is known as the *Rydberg constant*. Its value is 1.097×10^7 m^{-1}. This set of lines lies in the visible part of the electromagnetic spectrum and is called the **Balmer series.** The longest wavelength of the series, designated H_α line, is 6563 Å and the shortest wavelength, called the *series limit*, is 3646 Å. The longest wavelength corresponds to $n = 3$ and the shortest wavelength to $n = \infty$.

Subsequently, other series of lines were discovered for the hydrogen atom in different regions of the electromagnetic spectrum. These are known, after their discoverers, as the Lyman, the Paschen, the Brackett and the Pfund series. These are represented by the following formulae :

Lyman Series: Ultraviolet Region

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \quad n = 2, 3, 4,\ldots \tag{3.2}$$

Paschen Series: Infrared Region

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \quad n = 4, 5, 6,\ldots \tag{3.3}$$

Brackett Series : Infrared Region

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \quad n = 5, 6, 7,\ldots \tag{3.4}$$

Pfund Series : Infrared Region

$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right) \quad n = 6, 7, 8,\ldots \tag{3.5}$$

All the above formulae are special cases of the general formula

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \tag{3.6}$$

where n_1 and n_2 are positive integers with $n_1 < n_2$ and $n_2 = n_1 + 1, n_1 + 2,\ldots$. This is known as the **Rydberg-Ritz formula**.

It may be noted that the above formula expresses the wave number $(1/\lambda)$ of any line as the difference of two terms of the type

$$T_n = \frac{R}{n^2} \quad n = 1, 2,\ldots \tag{3.7}$$

It was pointed out by Ritz that the spectral lines of *all elements* can be obtained as the difference of two terms:

$$\boxed{\frac{1}{\lambda} = T_i - T_j} \tag{3.8}$$

Each term is characteristic of the particular atom. This statement is called the **Ritz combination principle**. However, for other atoms the terms T_i, T_j are generally more complicated than those for the hydrogen atom.

3.3 BOHR MODEL OF HYDROGENIC ATOMS

In 1913, a major step forward was taken by Niels Bohr. He suggested that the classical electromagnetic theory is not applicable to the processes at the atomic scale. He then combined Rutherford's nuclear model with the quantum idea of Planck and Einstein to develop a theory of hydrogenic atoms. The term "hydrogenic" is used for all one-electron atoms, i.e., the hydrogen atom and those ions which have only one electron, e.g., He^{+}, Li^{++}, Be^{+++} etc. These are also called *hydrogen-like atoms*. The theory was remarkably successful in explaining the observed spectrum of hydrogen.

Though Bohr's theory is incorrect and has now been replaced by the quantum mechanical treatment, it still remains an important milestone in the development of atomic physics and it is essential for the student to understand it before proceeding to the more correct theories.

The Bohr model is based on the following **postulates**:

1. The electron can revolve around the nucleus only in certain allowed circular orbits of definite energy and in these orbits it does not radiated. These orbits are called **stationary orbits**.
2. The angular momentum of the electron in a stationary orbit is an integral multiple of $\hbar (= h/2\pi)$, h being Planck's constant:

   $$l = mvr = n\hbar \tag{3.9}$$

   where m is the mass of the electron, v is its speed, r is the radius of the orbit and n is a positive integer.
3. The electron can make a transition from one orbit to another. The emission of radiation takes place as a single photon when an electron "jumps" from a higher orbit to a lower orbit. The frequency of the photon is

   $$\nu = \frac{E_2 - E_1}{h} \tag{3.10}$$

   where E_2 and E_1 are the energies of the electron in the higher and lower orbits, respectively. Conversely, an electron in the lower orbit can jump to the higher orbit by absorbing a photon of this frequency.

It may be noted that Bohr restricted to circular orbits for simplicity, even though elliptic orbits are also possible. Postulate 2 defines the discrete stationary orbits in terms of *quantization of angular momentum*. As we shall see below, this leads to the quantization of energy. Postulate 3, called *Bohr frequency rule*, takes care of the emission and absorption spectra of atoms.

The above postulates determine the possible values for the radii of the allowed circular orbits and the energies associated with these orbits. We do this below under the assumption that the electron moves around a stationary nucleus. This is a reasonable assumption because the nucleus, being very heavy as compared to the electron, can be assumed to have infinite mass. The correction due to the finite mass of the nuclues will be applied later.

Let Z be the atomic number of the nucleus. If e is the electronic charge, then the charge of the nucleus is Ze. The centripetal acceleration for circular motion is provided by the Coulomb attraction between the electron and the nucleus. Therefore,

$$\frac{mv^2}{r} = \frac{k(Ze)e}{r^2}$$

In SI system the constant k has the value 9×10^9 Nm^2/C^2. It is customary to replace it by $1/4\pi\varepsilon_0$, where ε_0 is the permittivity of vacuum, having value 8.85×10^{-12} C^2/Nm^2. Thus,

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} \tag{3.11}$$

From (3.9) and (3.11) we obtain the expressions for the **radius** of the nth *Bohr orbit* and the **speed** of the electron in this orbit, respectively, as

$$\boxed{r_n = \frac{(4\pi\varepsilon_0)\hbar^2 n^2}{Ze^2 m}} \tag{3.12}$$

and

$$\boxed{v_n = \frac{Ze^2}{(4\pi\varepsilon_0)\hbar n}} \tag{3.13}$$

The integer n is called the *quantum number*. Substituting the values of ε_0, $\hbar$, e, and m,

$$\boxed{r_n = 0.53\,\frac{n^2}{Z}\ \text{Å}} \tag{3.14}$$

and

$$\boxed{v_n = 2.18 \times 10^6\,\frac{Z}{n}\ \text{m/s}} \tag{3.15}$$

For the first Bohr orbit, also called the *ground state*, of hydrogen, $Z = 1$, $n = 1$. Therefore, the radius and the speed are 0.53 Å and 2.18×10^6 m/s, respectively. The first Bohr radius of hydrogen is generally denoted by the symbol a_0:

$$\boxed{a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{me^2}} \tag{3.16}$$

Energy of the Electron in the *n*th Bohr Orbit

The total energy E_n of the electron is the sum of the kinetic and potential energies:

$$E_n = \frac{1}{2}\, mv_n^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r_n}$$

$$= \frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} - \frac{m}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}$$

or
$$\boxed{E_n = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2}} \tag{3.17}$$

Sometimes it is convenient to express the energy in terms of the *Bohr radius* a_0. Using (3.16),

$$\boxed{E_n = -\frac{\hbar^2}{2ma_0^2}\frac{Z^2}{n^2}} \tag{3.18}$$

Substituting the values of the constants,

$$\boxed{E_n = -2.2 \times 10^{-18}\frac{Z^2}{n^2}\ \text{J} = -13.6\frac{Z^2}{n^2}\ \text{eV}} \tag{3.19}$$

This shows that the energy of the ground state of hydrogen is –13.6 eV. The negative sign indicates that the electron is bound. Energy will, therefore, be required to remove the electron infinite distance away from the nucleus. The minimum energy required to remove the electron from the ground state of hydrogen atom is 13.6 eV. This energy is, therefore, called the *ionization energy* of the hydrogen atom.

Frequency and Wavelength of the Radiation in the Transition $n_2 \rightarrow n_1$

Equation (3.10) gives the frequency of the radiation emitted when the electron makes a transition from an orbit of higher energy with quantum number n_2 to one of lower energy with quantum number n_1:

$$\nu = \frac{E_{n_2} - E_{n_1}}{h} = \frac{E_{n_2} - E_{n_1}}{2\pi\hbar}$$

Using (3.17) this becomes

$$\boxed{\nu = \frac{m}{4\pi\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \tag{3.20}$$

The inverse of the corresponding wavelength (λ), also called **wave number** ($\bar{\nu}$), is given by

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = \frac{m}{4\pi c\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \tag{3.21}$$

This can be written as

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = R_\infty Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \tag{3.22}$$

where

$$\boxed{R_\infty = \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2} \tag{3.23}$$

Equation (3.22) has the same form as the Rydberg-Ritz formula given in Equation (3.6). The constant R_∞ is obviously the Rydberg constant. The subscript "∞" is put to indicate that this derivation uses the infinite nuclear mass approximation. It now appears as a combination of fundamental constants. On substituting the values of the fundamental constants in (3.23), the value comes out to be very close to the empirical value 1.09737×10^7 m^{-1}. This agreement provides a direct confirmation of the Bohr model.

It is also clear that the "terms" in the Rydberg-Ritz formula are associated with the energies of the stationary states, which can take only discrete values.

3.4 EXPLANATION OF THE HYDROGEN SPECTRUM

In formula (3.22), if we put $Z = 1$, $n_1 = 1$ and $n_2 = 2, 3, 4, \ldots \infty$, we find that the values of λ so obtained agree with the experimentally observed wavelengths in the Lyman series. Thus, the Lyman series arises when the electron jumps from any of the higher orbits to the first orbit. Similarly, $n_1 = 2, 3, 4$ and 5 give, respectively, the Balmer, the Paschen, the Brackett and the Pfund series. In all the cases, the calculated values of λ agree with the corresponding experimental values.

Figure 3.1 shows the energy level diagram of hydrogen, also showing the transitions for the various spectral series. Conventionally, the Balmer lines are given the names H_α, H_β, H_γ, H_δ etc.

An atom normally remains in its ground state ($n = 1$). In order to make a transition to one of the higher states, the atom must be given energy by some external agency. The atom is then said to be in an excited state. The state with $n = 2$ is called the *first excited state*, that with $n = 3$ is called the *second excited state* and so on. The atom can be excited by collisions with electrons, photons, other hydrogen atoms etc. However, the atom cannot remain in an excited state for more than about 10^{-8} s. It falls back to a state of lower energy, emitting a photon in the process.

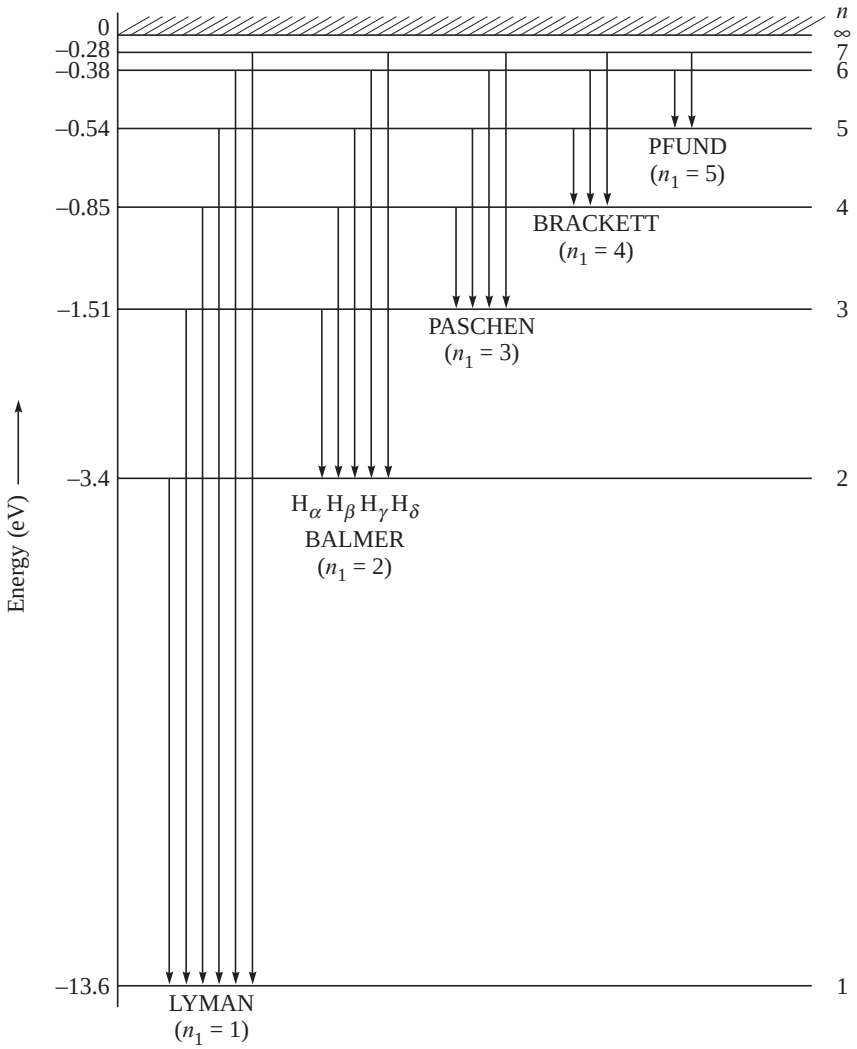


Figure 3.1 Energy level diagram for hydrogen.

Hydrogenic Ions

If we take $Z = 2, 3, 4,\ldots$ it is found that the Bohr model predicts correctly the energy levels and spectral lines of all the ions containing one electron. The calculated wavelengths agree closely with the observed values upto about $Z = 20$.

PROBLEM 3.1 The energy of an excited hydrogen atom is –3.4 eV. Calculate the angular momentum of the electron according to Bohr theory.

Solution: The energy of the electron in the *n*th orbit is

$$E_n = -\frac{13.6}{n^2}\ \text{eV}$$

Therefore,

$$n^2 = \frac{-13.6}{E_n} = \frac{-13.6}{-3.4} = 4$$

or $$n = 2$$

$$\text{Angular momentum} = \frac{nh}{2\pi}$$

$$= \frac{2 \times 6.63 \times 10^{-34}}{2 \times 3.14}$$

$$= \boxed{2.11 \times 10^{-34} \text{ Js}}$$

PROBLEM 3.2 The energy of the ground state of hydrogen atom is –13.6 eV. Find the energy of the photon emitted in the transition from $n = 4$ to $n = 2$.

Solution: $$E_{4\to 2} = 13.6\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

$$= 13.6\left[\frac{1}{4} - \frac{1}{16}\right] = \boxed{2.55 \text{ eV}}$$

PROBLEM 3.3 The H_α line of Balmer series is obtained from the transition $n = 3$ (energy = – 1.5 eV) to $n = 2$ (energy = – 3.4 eV). Calculate the wavelength for this line.

Solution: $$\frac{hc}{\lambda} = E_3 - E_2$$

or $$\lambda = \frac{hc}{E_3 - E_2}$$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{[-1.5 - (-3.4)] \times 1.6 \times 10^{-19}}$$

$$= \frac{6.6 \times 3 \times 10^{-7}}{1.9 \times 1.6}$$

$$= 6.513 \times 10^{-7} \text{ m}$$

$$= \boxed{6513 \text{ Å}}$$

PROBLEM 3.4 The first line of the Lyman series in the hydrogen spectrum has wavelength 1200 Å. Calculate the wavelength of the second line.

Solution: For the Lyman series

$$\frac{1}{\lambda} = R\left[1 - \frac{1}{n^2}\right], \; n = 2, 3, 4, \ldots$$

For the first line, $n = 2$. Therefore,

$$\frac{1}{\lambda_1} = R\left[1 - \frac{1}{4}\right] = \frac{3R}{4} \quad (1)$$

For the second line, $n = 3$. Therefore,

$$\frac{1}{\lambda_2} = R\left[1 - \frac{1}{9}\right] = \frac{8R}{9} \quad (2)$$

Dividing (1) by (2),

$$\frac{\lambda_2}{\lambda_1} = \frac{3}{4} \times \frac{9}{8} = \frac{27}{32}$$

or $$\lambda_2 = \frac{27}{32} \times 1200 = \boxed{1012.5 \text{ Å}}$$

PROBLEM 3.5 Find the longest and the shortest wavelengths of the Lyman series. Given, Rydberg constant = 1.097×10^7 m^{-1}.

Solution: For the Lyman series.

$$\frac{1}{\lambda} = R\left[1 - \frac{1}{n^2}\right]$$

For the longest wavelength, $n = 2$. Therefore,

$$\frac{1}{\lambda_{\text{longest}}} = R\left[1 - \frac{1}{4}\right] = \frac{3R}{4}$$

or $$\lambda_{\text{longest}} = \frac{4}{3 \times 1.097 \times 10^7}$$

$$= 1.215 \times 10^{-7} \text{ m} = \boxed{1215 \text{ Å}}$$

For the shortest wavelength, $n = \infty$. Therefore,

$$\frac{1}{\lambda_{\text{shortest}}} = R[1 - 0] = R$$

or $$\lambda_{\text{shortest}} = \frac{1}{1.097 \times 10^7} = 0.911 \times 10^{-7} \text{ m}$$

$$= \boxed{911 \text{ Å}}$$

PROBLEM 3.6 A hydrogen-like atom has one electron revolving around a stationary nucleus. The energy required to excite the electron from the second orbit to the third orbit is 47.2 eV. What is the atomic number of the atom?

Solution: $47.2 = 13.6Z^2\left[\frac{1}{4} - \frac{1}{9}\right]$

Solving, $\boxed{Z = 5}$

PROBLEM 3.7 Which state of the triply ionized beryllium has the same orbital radius as that of the ground state of hydrogen? Compare the energies of the two states.

Solution: We have $r_n \propto \frac{n^2}{Z}$

For the ground state of hydrogen, $Z = 1$, $n = 1$
For Be^{+++}, $Z = 4$, $n = ?$
Since the two radii are equal,

$$\left(\frac{n^2}{Z}\right)_{Be^{+++}} = \left(\frac{n^2}{Z}\right)_{H}$$

$$\Rightarrow \quad \frac{n^2_{Be^{+++}}}{4} = \frac{1}{1}$$

or $$n_{Be^{+++}} = \boxed{2}$$

Now $$E_n \propto \frac{Z^2}{n^2}$$

$$\Rightarrow \quad \frac{E_2(Be^{+++})}{E_1(H)} = \frac{4^2/2^2}{1^2/1^2} = \boxed{4}$$

PROBLEM 3.8 Which state of doubly ionized lithium has the same energy as the ground state energy of the hydrogen atom? Compare the orbital radii of the two states.

Solution: We have $E_n \propto \frac{Z^2}{n^2}$

For Li^{++}, $Z = 3$. Therefore, *the n = 3 state of Li^{++} has the same energy as the n = 1 state of hydrogen.*

Now $$r_n \propto \frac{n^2}{Z}$$

Therefore $$\frac{r_3(Li^{+++})}{r_1(H)} = \frac{3^2/3}{1/1} = \boxed{3}$$

PROBLEM 3.9 Hydrogen atom in its ground state is excited by means of a monochromatic radiation of wavelength 970.6 Å. How many different wavelengths are possible in the resulting emission spectrum? Find the longest wavelength amongst these.

Solution: Energy of the radiation quantum

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{970.6 \times 10^{-10} \times 1.6 \times 10^{-19}} = 12.75 \text{ eV}$$

Energy of the excited state

$$E_n = -13.6 + 12.75 = -0.85 \text{ eV}$$

Now, we know that $E_n = -\dfrac{13.6}{n^2}$

or $n^2 = -\dfrac{13.6}{E_n} = \dfrac{-13.6}{-0.85} = 16$

or $n = \boxed{4}$

The number of possible transition in going to the ground state, and hence the number of different wavelengths in the spectrum, will be **six** as shown in Figure. 3.2.

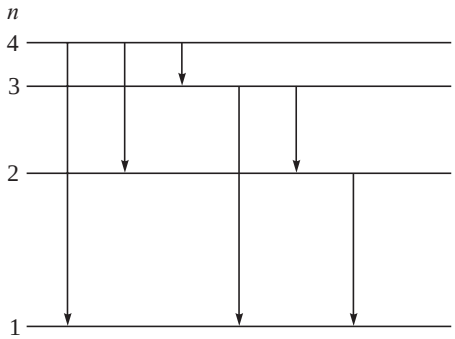


Fig. 3.2 Transitions from the excited state having $n = 4$.

The longest wavelength corresponds to the minimum energy difference, *i.e.*, to the transition $4 \rightarrow 3$.

Now $E_3 = -\dfrac{13.6}{3^2} = -1.51 \text{ eV}$

$$\frac{hc}{\lambda_{\max}} = E_4 - E_3$$

or $$\lambda_{\max} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{(1.51 - 0.85) \times 1.6 \times 10^{-19}}$$

$$= 18.75 \times 10^{-7} \text{ m}$$

$$= \boxed{18{,}750 \text{ Å}}$$

PROBLEM 3.10 In a singly-ionized helium atom the electron is in the third orbit. A photon of energy 10.04 eV knocks out the electron. Calculate the stopping potential of the electron. The ionization energy of hydrogen atom is 13.6 eV.

Solution: For He^+, $Z = 2$.

Therefore, ionization energy of $He^+ = (2)^2 \times 13.6 = 54.4$ eV

Energy of the electron in the first orbit

$$E_1 = -54.4 \text{ eV}$$

Energy of the electron in the third orbit

$$E_3 = \frac{E_1}{(3)^2} = -\frac{54.4}{9} = -6.04 \text{ eV}$$

Energy of the incident photon = 10.04 eV
Therefore, the energy of the knocked out electron

$$= 10.04 - 6.04 = 4.0 \text{ eV}$$

Hence, required stopping potential = $\boxed{4.0 \text{ V}}$

PROBLEM 3.11 The ionization energy of a hydrogen-like atom is 4 rydberg. Find the wavelength of the radiation emitted when the electron jumps from the first excited state to the ground state.

$$1 \text{ rydberg} = 2.2 \times 10^{-18} \text{ J}; \; h = 6.6 \times 10^{-34} \text{ Js}.$$

Solution: Ionization energy $= 4 \times 2.2 \times 10^{-18}$

$$= 8.8 \times 10^{-18} \text{ J}$$

Energy of the electron in the ground state ($n = 1$)

$$E_1 = -8.8 \times 10^{-18} \text{ J}$$

Energy of the electron in the first excited state ($n = 2$)

$$E_2 = \frac{E_1}{(2)^2} = -2.2 \times 10^{-18} \text{ J}$$

If λ is the wavelength of the radiation emitted in the transition $n = 2 \rightarrow n = 1$, then

$$\frac{hc}{\lambda} = E_2 - E_1$$

or

$$\lambda = \frac{hc}{E_2 - E_1}$$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{(8.8 - 2.2) \times 10^{-18}}$$

$$= 3.0 \times 10^{-8} \text{ m}$$

$$= \boxed{300 \text{ Å}}$$

PROBLEM 3.12 A beam of electrons bombards a sample of hydrogen. Through what potential difference must the beam be accelerated if the second line of Lyman series is to be emitted?

Solution: The second line of Lyman series is emitted in the transition $n = 3 \rightarrow n = 1$.

Binding energy of the atom in the $n = 1$ state

$$= 13.6 \text{ eV}$$

Binding energy of the atom in the $n = 3$ state

$$= \frac{13.6}{(3)^2} = 1.51 \text{ eV}$$

Energy required for the atomic electron to jump from the $n = 1$ state to the $n = 3$ state

$$= 13.6 - 1.51 = 12.09 \text{ eV}$$

The electron beam must, therefore, be accelerated through **a potential difference of 12.09 V**. When an electron in the beam collides with the atom, it would raise the electron in the atom from the $n = 1$ state to the $n = 3$ state. When this electron returns back to the ground state, the second line of the Lyman series would be emitted.

3.5 CORRECTION FOR FINITE NUCLEAR MASS

So far we have assumed that the nucleus has infinite mass and, therefore, remains stationary. This is a reasonable assumption because the nuclear masses are much larger than the electronic mass. However, there are certain finer details of spectra which depend on the actual mass of the nucleus. Since the nucleus has finite mass, both the electron and the nucleus move about their common centre of mass with the same angular velocity. It can be shown, using Newtonian mechanics, that the effect of nuclear motion can be taken care of by replacing the electronic mass m by the *reduced mass* μ of the electron-nucleus system, given by

$$\boxed{\mu = \frac{mM}{m + M}} \tag{3.24}$$

where M is the mass of the nucleus. The *Rydberg constant* for hydrogen will then be

$$\boxed{R_H = \frac{M_H}{m + M_H} R_\infty = \frac{R_\infty}{1 + m/M_H}} \tag{3.25}$$

The numerical value comes out to be 1.09678×10^7 m^{-1} which is closer to the empirical value 1.096776×10^7 m^{-1} than R_∞.

In general, for atom X,

$$\boxed{R_X = \frac{R_\infty}{1 + m/M_X}} \tag{3.26}$$

where M_X is the mass of the nucleus of X. Thus,

$$\boxed{\frac{R_X}{R_H} = \frac{1 + m/M_H}{1 + m/M_X}} \tag{3.27}$$

Although the ratio R_∞/R_x is very nearly unity, the small difference has some interesting spectroscopically observable consequences. We mention two of these.

First, consider He^+. The wave number formula (3.22) which contains R_∞ and hence is independent of the nuclear mass, predicts that, for given n_1 and n_2, the wave number of the spectral line of singly ionized helium should be four times as large as the wave number of the corresponding line of hydrogen. Actual spectrum showed some disprepancy which was explained by Bohr by taking into account the finite nuclear masses.

Second, consider deuterium (H^2), which is an isotope of hydrogen having mass double that of hydrogen (H^1). Equation (3.22) predicts that both H^2 and H^1 should have identical spectra. However, the spectral lines of H^2 are slightly shifted with respect to the corresponding lines of H^1. The ratio of the frequencies of the corresponding lines is 1.00027, which is small but detectable. The existence of deuteron was proved by Urey and coworkers through this shift.

PROBLEM 3.13 The Rydberg constant for hydrogen is $1.09678 \times 10^7\ m^{-1}$ and that for singly ionized helium is $1.09722 \times 10^7\ m^{-1}$. Given that the mass of the helium nucleus is four times that of the hydrogen nucleus, calculate the ratio of the electron mass to the proton mass.

Solution: The hydrogen nucleus is proton. We have, using (3.27)

$$\frac{R_{He}}{R_H} = \frac{1+(m/M_H)}{1+(m/M_{He})}$$

$$= \frac{1+(m/M_H)}{1+(m/4M_H)}$$

or $$R_{He} + R_{He}\frac{m}{4M_H} = R_H + R_H\frac{m}{M_H}$$

or $$\frac{m}{M_H} = \frac{R_{He} - R_H}{R_H - (R_{He}/4)}$$

$$= \frac{1.09722 - 1.09678}{1.09678 - (1.09722/4)}$$

$$= \boxed{\frac{1}{1869}}$$

3.6 LIMITATIONS OF THE BOHR MODEL. SOMMERFELD'S ELLIPTIC ORBITS

In spite of the impressive success of Bohr's theory in obtaining the correct values of the Rydberg constant and the wavelengths of the spectral lines of hydrogenic atoms, the model had serious limitations and shortcomings.

First, it cannot be generalized to explain the structure and spectra of atoms containing two or more electrons.

Second, it cannot explain the differences in the intensities of spectral lines.

Third, spectrometers of high resolving power show that some spectral lines in fact consist of a group of closely spaced lines. Bohr theory cannot explain this *fine structure* of spectral lines.

Fourth, this model cannot be applied to unbound systems and scattering problems.

Bohr's assumption of circular orbits was an oversimplication because elliptic orbits are possible under the inverse-square Coulomb force. Wilson (1915) and Sommerfeld (1916) replaced Bohr's quantization of angular momentum by a more general postulate and Sommerfeld used it to develop a more general theory which included *elliptic orbits*. The new postulate quantizes the *phase integral*:

$$\boxed{\oint p_i \, dq_i = n_i h, \quad n_i = 0, 1, 2, \ldots} \tag{3.28}$$

where p_i is the momentum conjugate to the coordinate q_i. The integration is taken over a complete period of the motion.

For an electron moving in an elliptic orbit around the nucleus (Fig. 3.3), Equation (3.28) gives the two conditions

$$\oint p_r dr = n_r h \tag{3.29a}$$

and

$$\oint p_\phi d\phi = n_\phi h \tag{3.29b}$$

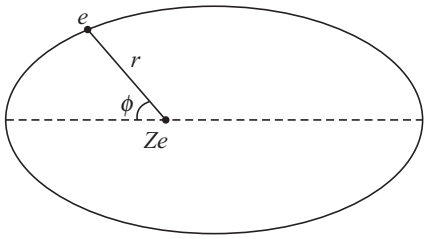


Figure 3.3 Electron moving in an elliptic orbit.

p_ϕ is the angular momentum which is constant. Therefore, (3.29b) yields

$$p_\phi(2\pi) = n_\phi h$$

or

$$p_\phi = n_\phi h$$

which is Bohr's second postulate. n_ϕ is called the *angular* or *azimuthal* quantum number and n_r the *radial* quantum number. The sum

$$n = n_r + n_\phi \tag{3.30}$$

is called the *principal* quantum number. Sommerfeld found that Bohr's energy expression (3.17) holds for elliptic orbits, with n being the principal quantum

number. That is, the energy depends only on n. Now, for a given n there are several orbits corresponding to those sets of values of n_r and n_ϕ for which $n_r + n_\phi = n$. Out of these orbits, there is one which is circular—that for which $n_r = 0$ and $n_\phi = n$. This explains why Bohr's model, which considered only circular orbits, was successful.

If a number of quantum states have the same energy, they are said to be *degenerate*. Thus, here all the states with the same principal quantum number are degenerate. Sommerfeld made an attempt to remove this degeneracy, and hence explain the fine structure of spectral lines, by taking into account the relativistic mass variation of the electron. However, it was soon realized that Sommerfeld's theory is not the correct explanation of the fine structure. We now know that it is due to the fact that electron has intrinsic spin which gives rise to spin-orbit interaction.

Bohr-Sommerfeld theory is now known as the **old quantum theory**. It could be applied only to some periodic systems. Very soon it was superseded by quantum mechanics developed by Schrödinger, Heisenberg, Born and others based on the discovery of the wave nature of matter by de Broglie.

3.7 THE FRANCK-HERTZ EXPERIMENT

The Bohr theory predicted the existence of discrete energy levels in atoms. Soon after Bohr's work, in 1914, a direct experimental confirmation of this was provided by Frank and Hertz. They demonstrated, in a rather simple and elegant manner, that energy is absorbed by atoms in discrete quanta. Frank and Hertz received the 1925 Nobel Prize in Physics.

A schematic diagram of the apparatus used in the experiment is shown in Figure 3.4. It consists of a tube fitted with a cathode C, an accelerating grid G and a collecting plate P. The cathode emits electrons when heated electrically. The grid is located near the plate. A variable voltage V is applied between the cathode and the grid, making the grid positive with respect to the cathode, so that the electrons are accelerated towards the grid. The plate is given a small retarding potential ΔV with respect to the grid. This prevents the electrons with very small kinetic energy from reaching the plate, so that these electrons may not contribute to the plate current.

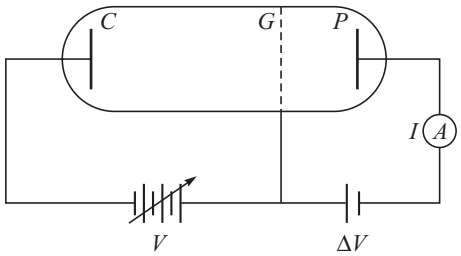


Figure 3.4 Schematic diagram of the Franck-Hertz experiment.

The tube was filled with mercury vapour. The accelerating potential V was gradually increased from zero and the current I was measured continuously. The graph between I and V is shown in Figure 3.5. As the accelerating voltage V was increased, the current also increased. However, at a certain voltage V_0 = 4.9 V, the current dropped sharply and started increasing again. This behaviour is repeated at integral multiples of V_0.

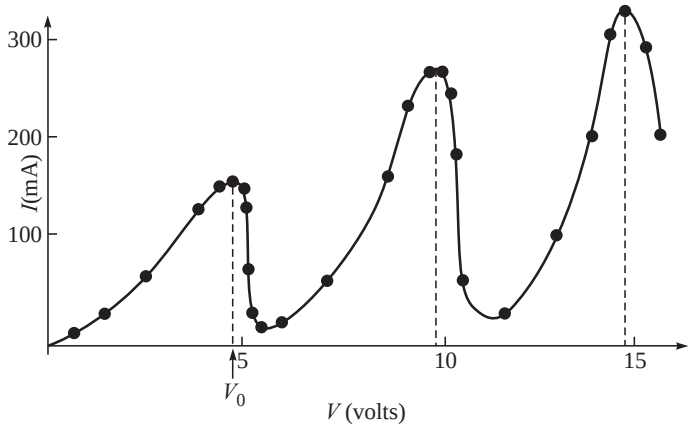


Figure 3.5 Variation of the current I as a function of the accelerating voltage V in the Franck-Hertz experiment.

The phenomenon can be explained as follows. As the voltage is increased from zero, the speed of the electrons increases and, therefore, the current increases. Of course, on their way to the plate, the electrons collide elastically with the mercury atoms. But the atoms are relatively too heavy, and therefore, the electrons lose negligible kinetic energy in the collision. However, at a certain potential V_0, the kinetic energy of the electron becomes exactly equal to the difference in energies between the ground state and the first excited state of mercury. The electron then gives up all its energy to excite the atom and the current falls sharply. The electron then moves to accelerate through the tube again and the process gets repeated when it again acquires an energy of 4.9 eV.

Now, as soon as an atom gets excited, it returns back to the ground state by emitting a photon. In this case, the photon will have energy 4.9 eV, which corresponds to a wavelength of 2536 Å. Franck and Hertz found that when the accelerating potential was less than 4.9 V no lines were observed in the spectrum of mercury. Above this potential, a strong emission line appeared, with wavelength 2536 Å. Thus, the Franck-Hertz experiment confirmed the existence of discrete energy levels in atoms.

3.8 THE CORRESPONDENCE PRINCIPLE

Bohr formulated the correspondence principle in 1923 to serve as a guide in the development of quantum theory. It states that *the quantum theory should agree with classical physics in the limit in which quantum effects become insignificant*.

To formulate the principle mathematically, we note that the classical limit is attained when the quantized variables are much larger then their minimum quantum size. Consider the case of the hydrogen atom. In Bohr's model, the angular momentum l of the electron is $n\hbar$, where n is an integer. The minimum quantum size is $\hbar$. Obviously, the classical limit means that $l >> \hbar$, which effectively means that n is large.

Since the energy of a Bohr orbit is proportional to $1/n^2$, for large values of n the energy levels are so close together that they become indistinguishable and can be considered to have a continuous range of values for all practical purposes. Thus, the correspondence principle can be restated mathematically as: *The quantum theory must approach classical theory in the limit $n \to \infty$, where n is a quantum number.*

The correspondence principle inspired most of Bohr's work and has played an important role in the initial development of quantum theory. It even helped and motivated Heisenberg in developing his version of quantum mechanics.

An important application of the correspondence principle is in deriving the **selection rules**, which are restricting on the type of transitions that the atom can make. Consider the transition from the state with quantum number $n + k$ to the state with quantum number n, in Bohr's theory. The frequency of the emitted photon is [Equation 3.20],

$$\nu = \frac{m}{4\pi\hbar^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left[\frac{1}{n^2} - \frac{1}{(n+k)^2}\right]$$

For large n, that is for $n >> k$, we may write

$$\frac{1}{(n+k)^2} \approx \frac{1}{n^2(1+k/n)^2}$$

$$= (1/n^2)(1 - 2k/n) = \frac{1}{n^2} - \frac{2k}{n^3}$$

Therefore,

$$\nu = \frac{m}{4\pi}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{2k}{(n\hbar)^3}$$

Substituting $l = n\hbar$, where l is the angular momentum of the electron in the nth state, we get

$$\nu = \frac{m}{2\pi l^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 k \tag{3.31}$$

Now, according to classical electrodynamics, a revolving charged particle emits radiation of frequency equal to the frequency of revolution. Thus, the classical frequency of the radiation emitted by an electron revolving with speed v in a circular orbit of radius r is given by

$$\nu_{\text{cl}} = \frac{v}{2\pi r}$$

Using Equation (3.12) and (3.13), this become

$$\nu_{cl} = \frac{m}{2\pi l^3}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \tag{3.32}$$

Comparing (3.31) and (3.32), we find that $\nu = \nu_{cl}$ provided $k = 1$. Thus, for large n, transitions are possible only between adjacent states.

Using this as a guide, Bohr asserted that *all transitions, irrespectively of the value of n, are governed by the rule*: $\boldsymbol{\Delta n = 1}$. Thus, correspondence principle leads us to the proper selection rule.

If we analyze the spectral series of hydrogen, we find that the transitions are not restricted by this selection rule. However, if we look at the intensities of the spectral lines, we find that the lines corresponding to the $\Delta n = 1$ transitions are the most intense. Thus, the selection rule obtained using the correspondence principle agrees with the experiment approximately.

SUMMARY

1. In order to explain the results of the alpha-scattering experiment, Rutherford proposed the nuclear model of the atom. This model is not stable according to classical electrodynamics. Moreover, it cannot account for the characteristic line spectra of elements.

2. Bohr postulated that an electron in an atom can revolve in certain *stationary orbits* without radiating. In these orbits the angular momentum of the electron is an integral multiple of $\hbar$.

3. Bohr further postulated that a photon is emitted or absorbed by the atom when an electron jumps from one orbit to another. The frequency of the photon is $\Delta E/h$, where ΔE is the energy difference between the two states.

4. Using these postulates Bohr was able to predict the wavelengths of the spectral lines of hydrogenic atoms reasonably well.

5. Slight discrepancies in spectra were explained by taking into account the finite mass of the nucleus.

6. Bohr's model had serious limitations. It could not explain the fine structure and the differences in the intensities of spectral lines and could not be extended to atoms containing more than one electron.

7. Wilson and Sommerfeld attempted to developed a more general theory by quantizing the phase integral:

$$\oint p_i dq_i = n_i h, \quad n_i = 0, 1, 2,\ldots$$

where p_i is the momentum conjugate to the coordinate q_i.
However, their theory, called the old quantum theory, could be applied only to some periodic systems. It was soon superseded by a more satisfactory quantum mechanics.

8. Franck and Hertz demonstrated, by a simple and elegant experiment, that energy is absorbed by atoms in discrete quanta.

9. Bohr formulated the correspondence principle which states that the quantum theory should agree with classical physics in the limit in which quantum effects become insignificant, that is, in the limit $n \to \infty$. This principle served as a guide in the development of quantum mechanics.

QUESTIONS

1. State the postulates of Bohr's theory of hydrogenic atoms. Using these postulates derive the expressions for (a) the radius of the *n*th orbit, (b) the velocity of the electron in the *n*th orbit, (c) the energy of the electron in the *n*th orbit, (d) the frequency and wavelength of the radiation in the transition $n_2 \to n_1$.

2. Give an explanation of the spectrum of hydrogen on the basis of the Bohr model. Express Rydberg constant in terms of fundamental constants. Draw the energy level diagram of hydrogen, indicating the energies of the first few states in eV.

3. Obtain the modified Bohr formula for the wavelength of a spectral line taking into consideration the nuclear mass. Explain how this modification helped in (a) explaining the spectrum of He^+ and (b) the discovery of deuterium.

4. What are the limitations of Bohr's theory?

5. Describe the Franck-Hertz experiment. What conclusion was drawn from it?

6. State Bohr's correspondence principle. Explain how does it guide in obtaining the selection rule for atomic transitions.

EXERCISES

1. The first line of the Balmer series has wavelength 6563 Å. Calculate the wavelength of (a) the second line of the Balmer series, and (b) the first line of the Lyman series. [***Ans.*** (a) 4861.5 Å, (b) 1215 Å]

2. Find the shortest and the longest wavelengths of the Balmer series. Rydberg constant = 1.097×10^7 m^{-1}. [***Ans.*** 3645 Å, 6563 Å]

3. A photon incident upon a hydrogen atom ejects an electron with a kinetic energy of 9.2 eV. If the ejected electron was in the first excited state, calculate the energy of the photon. [***Ans.*** 12.6 eV]

4. A hydrogen atom in its ground state absorbs a photon of wavelength 180 nm. Will the electron be excited to another level, or will it be set free?

[**Hint.** Energy of the photon = 6.9 eV; Energy required to excite the electron to the next state = 10.2 eV. Since 6.9 < 10.2, the electron cannot be excited.]

5. Find the ratio of the Rydberg constants for deuterium and hydrogen.

Given, $\frac{\text{Mass of proton}}{\text{Mass of electron}} = 1836.$ [***Ans.*** 1.00027]

Chapter

4

Wave Nature of Matter and the Need for a Wave Function

Chapter Contents

4.1 De Broglie's Hypothesis
4.2 Experimental Verification of De Broglie's Hypothesis
4.3 The Double-Slit Experiment with Particles
4.4 The Need for a Wave Function
4.5 Born's Interpretation of the Wave Function

4.1 DE BROGLIE'S HYPOTHESIS

In Chapter 2 we studied that after the work of Planck, Einstein and Compton, it was established that radiation has dual nature. That is, it acts like a wave in some situations and as a particle in some other situations. In 1924, Louis de Broglie extended this wave-particle duality to material particles. He was guided by the intuitive feeling that nature loves symmetry. Nature has two entities—matter and radiation. Therefore, if radiation has particle-like properties, then material particles (electron, proton, neutron etc.) should possess wave-like properties.

We have seen that a photon of frequency ν has energy

$$E = h\nu$$

and momentum

$$p = \frac{E}{c} = \frac{h\nu}{c}$$

In terms of wavelength this can be written as

$$p = \frac{h}{\lambda}$$

De Broglie proposed that this relation applies to material particles as well as photons. Thus, de Broglie postulated that *with every material particle a wave is associated, having wavelength*

$$\boxed{\lambda = \frac{h}{p} \quad \textbf{(De Broglie wavelength)}} \tag{4.1}$$

For a particle of mass m, moving with a speed v, this becomes

$$\boxed{\lambda = \frac{h}{mv}} \tag{4.2}$$

For a relativistic particle, m is the rest mass multiplied by $[1 - v^2/c^2]^{-1/2}$.

This is called **de Broglie's hypothesis** and λ is called the *de Broglie wavelength*. The associated wave is called *matter wave* or *de Broglie wave* or *pilot wave*. It is worth noting that, unlike Planck's hypothesis, de Broglie's hypothesis, when proposed, had no supporting experimental evidence. Such evidence came three years later in 1927. However, de Broglie was motivated by the mystery that surrounded the Bohr postulate for stationary orbits. He attempted to explain the stationary Bohr orbits by fitting a standing wave around the circumference of an orbit (Figure 4.1). If λ is the wavelength associated with the nth orbit and r is its radius, then it must be required that

$$2\pi r = n\lambda$$

Combining this with the Bohr postulate

$$mvr = \frac{nh}{2\pi}$$

we get

$$n\lambda = 2\pi\left(\frac{nh}{2\pi mv}\right)$$

or

$$\lambda = \frac{h}{mv}$$

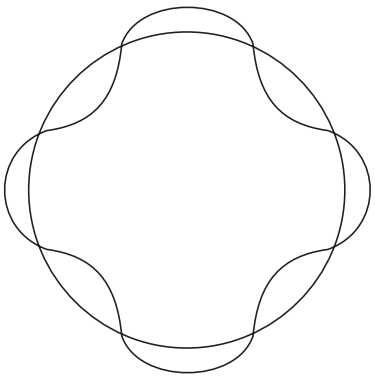


Figure 4.1 De Broglie wave for $n = 4$ Bohr orbit.

De Broglie was also guided by the analogy of the least-action principle in mechanics and Fermat's principle in optics. We shall not go into the details of this.

We may write

$$p = \frac{h}{\lambda} = \hbar k$$

where $k = 2\pi/\lambda$. Thus, the two basic relations of quantum theory are

$$E = \hbar\omega \tag{4.3}$$

and

$$\mathbf{p} = \hbar\mathbf{k} \tag{4.4}$$

(Basic relations of quantum theory)

The vector **k** is called the *propagation vector*. De Broglie could not provide a proper interpretation to the concept of matter waves. Nor could Schrödinger, who developed the wave mechanics of particles based on de Broglie's idea. What is believed to be the correct interpretation of the "wavyness" associated with a particle was given by Max Born in 1927. This will be discussed in detail later.

Other Useful Expressions for the De Broglie Wavelength

Nonrelativistic

In terms of Kinetic Energy:

For a nonrelativistic particle of mass m having kinetic energy K,

$$K = \frac{p^2}{2m}$$

or

$$p = \sqrt{2mK}$$

Therefore, the de Broglie wavelength can be expressed as

$$\lambda = \frac{h}{\sqrt{2mK}} \tag{4.5}$$

In terms of Accelerating Potential:

If a particle of mass m and charge q is accelerated through a potential difference V, then

$$K = qV$$

Therefore,

$$\lambda = \frac{h}{\sqrt{2mqV}} \tag{4.6}$$

For an electron this yields

$$\lambda = \left(\frac{6.625\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-19}}}\right)\frac{1}{\sqrt{V}}$$

$$= \frac{12.3 \times 10^{-10}}{\sqrt{V}} \text{ m}$$

or
$$\boxed{\lambda = \frac{12.3}{\sqrt{V}} \text{ Å}} \tag{4.7}$$

Relativistic

In terms of Kinetic Energy:

For a particle of rest mass m_0, the total energy E is given by

$$E^2 = p^2c^2 + m_0^2 c^4$$

or
$$p = \frac{1}{c}\sqrt{E^2 - m_0^2 c^4}$$

If K is the kinetic energy of the particle, then

$$E = K + m_0c^2$$

Therefore,

$$p = \frac{1}{c}\sqrt{(K + m_0c^2)^2 - m_0^2c^4}$$

$$= \frac{1}{c}\sqrt{K(K + 2m_0c^2)}$$

The de Broglie wavelength is

$$\boxed{\lambda = \frac{h}{p} = \frac{hc}{\sqrt{K(K + 2m_0c^2)}}} \tag{4.8}$$

In terms of Accelerating Potential:

If a particle has charge q and is accelerated through a potential difference V, then

$$K = qV$$

Substituting in Eq. (4.8),

$$\lambda = \frac{hc}{\sqrt{qV(2m_0c^2 + qV)}}$$

$$= \frac{h}{\sqrt{2m_0qV\left(1 + \dfrac{qV}{2m_0c^2}\right)}}$$

or
$$\boxed{\lambda = \frac{h}{\sqrt{2m_0qV\left(1 + \dfrac{\alpha}{2}\right)}},\ \alpha = \frac{qV}{m_0c^2}} \tag{4.9}$$

For an electron this yields

$$\boxed{\lambda = \frac{12.3}{\sqrt{V\left(1+\frac{\alpha}{2}\right)}}\text{ Å}} \tag{4.10}$$

PROBLEM 4.1 Find the de Broglie wavelength of electrons accelerated through a potential difference of 100 volt.

Solution: For electrons accelerated through a potential difference V, the de Broglie wavelength is given by

$$\lambda = \frac{h}{\sqrt{2me}} \cdot \frac{1}{\sqrt{V}} = \frac{12.3}{\sqrt{V}} \text{ Å}$$

For $V = 100$ volt

$$\lambda = \frac{12.3}{\sqrt{100}} = \boxed{1.23 \text{ Å}}$$

PROBLEM 4.2 Find the de Broglie wavelength of electrons moving with a kinetic energy of 100 eV.

Solution: $$\lambda = \frac{h}{\sqrt{2mK}} = \frac{6.63\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times100\times1.6\times10^{-19}}}$$

$$= \boxed{1.2\times10^{-10} \text{ m}}$$

PROBLEM 4.3 What should be the kinetic energy of a neutron in eV so that its associated de Broglie wavelength is 1.4×10^{-10} m? Mass of neutron = 1.675×10^{-27} kg.

Solution: $$\lambda = \frac{h}{\sqrt{2mK}} \quad \text{or} \quad K = \frac{h^2}{2m\lambda^2}$$

$$= \frac{(6.63\times10^{-34})^2}{2\times1.675\times10^{-27}\times(1.4\times10^{-10})^2}$$

$$= 6.634 \times 10^{-21}\text{J}$$

$$= \boxed{4.15\times10^{-2} \text{ eV}}$$

PROBLEM 4.4 An electron, in a hydrogen-like atom, is in an excited state. It has a total energy of –3.4 eV. Calculate (a) the kinetic energy and (b) the de Broglie wavelength of the electron.

Solution: (a) We know that for an electron in orbit in a hydrogen-like atom

Kinetic energy $K = -$(Total energy E)

Here $E = -3.4$ eV

Therefore, $K = -(-3.4)$

$= 3.4$ eV

(b) de Broglie wavelength

$$\lambda = \frac{h}{\sqrt{2mK}} = \frac{6.63\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times3.4\times1.6\times10^{-19}}}$$

$$= 6.663 \times 10^{-10} \text{ m} = \boxed{6.663 \text{ Å}}$$

PROBLEM 4.5 Find the kinetic energy of a neutron in electron-volt if its de Broglie wavelength is 1.0 Å. Mass of neutron = 1.674×10^{-27} kg; $h = 6.60 \times 10^{-34}$ Js.

Solution: $\lambda = \dfrac{h}{\sqrt{2mK}}$

or $K = \dfrac{h^2}{2m\lambda^2}$

$$= \frac{(6.6\times10^{-34})^2}{2\times1.674\times10^{-27}\times(1.0\times10^{-10})^2}$$

$$= 13.01 \times 10^{-21} \text{ J}$$

$$= \frac{13.01\times10^{-21}}{1.6\times10^{-19}} \text{ eV}$$

$$= \boxed{8.13\times10^{-2} \text{ eV}}$$

PROBLEM 4.6 A ball of mass 10 g is moving with a speed of 1m/s. Calculate the de Broglie wavelength associated with it. Can the effect of this wavelength be observed experimentally?

Solution: $\lambda = \dfrac{h}{mv}$

$$= \frac{6.63\times10^{-34}}{10\times10^{-3}\times1}$$

$$= \boxed{6.63\times10^{-32} \text{ m}}$$

This wavelength is negligible compared to the dimensions of the ball. Therefore its effect *cannot be observed*.

PROBLEM 4.7 Calculate the de Broglie wavelength of thermal neutrons at 27°C. Given Boltzmann constant $k = 1.38 \times 10^{-23}$ J/K.

Solution: We have

$$\lambda = \frac{h}{\sqrt{2mK}}$$

$$= \frac{h}{\sqrt{2mkT}}$$

where T is the absolute temperature. Substituting the values

$$\lambda = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300}}$$

$$= 1.78 \times 10^{-10} \text{ m} = \boxed{1.78 \text{ Å}}$$

PROBLEM 4.8 A proton and a deuteron have the same kinetic energy. Which of the two has longer de Broglie wavelength?

Solution: Let m be the mass of the proton. Then the mass of the deuteron is $2m$. We have

$$\lambda_{\text{proton}} = \frac{h}{\sqrt{2mK}}$$

and

$$\lambda_{\text{deuteron}} = \frac{h}{\sqrt{2(2m)K}}$$

Dividing,

$$\frac{\lambda_{\text{proton}}}{\lambda_{\text{deuteron}}} = \boxed{\sqrt{2}}$$

PROBLEM 4.9 Show that the de Broglie wavelength of an electron is equal to its Compton wavelength when its speed is $c/\sqrt{2}$, c being the speed of light.

Solution:

$$\lambda = \frac{h}{mv}$$

$$= \frac{h}{m_0 v}\left(1 - v^2/c^2\right)^{\frac{1}{2}}$$

$$= \left(\frac{h}{m_0 c}\right)\left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}} \frac{c}{v}$$

When $v = c/\sqrt{2}$,

$$\lambda = \left(\frac{h}{m_0 c}\right)\left(1 - \frac{1}{2}\right)^{\frac{1}{2}} (\sqrt{2})$$

or

$$\boxed{\lambda = \frac{h}{m_0 c}}$$

which is the Compton wavelength of the electron.

4.2 EXPERIMENTAL VERIFICATION OF DE BROGLIE'S HYPOTHESIS

In Problem 4.1 we found that the de Broglie wavelength of electrons, accelerated through a potential difference of 100 V, is 1.23 Å. This is of the order of the distance between atomic planes in crystals. This fact suggests that the existence of matter waves may be demonstrated by using crystals as diffraction gratings for electrons in a manner similar to X-ray diffraction by crystals. Such experiments were performed in 1927 by Davisson and Germer, and independently by G.P. Thomson. We discuss these below.

Davisson-Germer Experiment

The experimental arrangement is shown in Figure 4.2. A narrow beam of electrons, accelerated through a potential difference V, was directed normally towards the surface of a nickel crystal. The electrons were scattered in all directions by the atoms in the crystal. The intensity of the scattered electrons was measured as a function of the latitude angle ϕ measured from the axis of the incident beam for different accelerating potentials. Figure 4.3 shows the polar graph of the variation of the intensity with ϕ for $V = 54$ volts. At each angle,

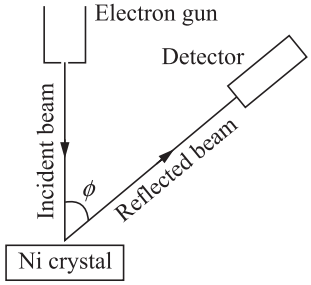


Figure 4.2 Schematic diagram of the Davisson-Germer experiment.

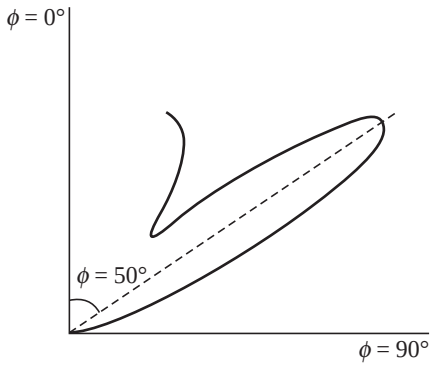


Figure 4.3 Polar plot of the intensity as a function of the scattering angle for 54 eV electrons.

the intensity is given by the distance of the point from the origin. It is seen that as ϕ increases from zero, the intensity first decreases, passes through a minimum at about 35° and then rises to a peak value at 50°. The occurrence of this peak can be explained as being due to constructive interference of the electron waves reflected from some particular set of "Bragg" planes in the crystal lattice as in the case of X-rays. This is shown in Figure 4.4.

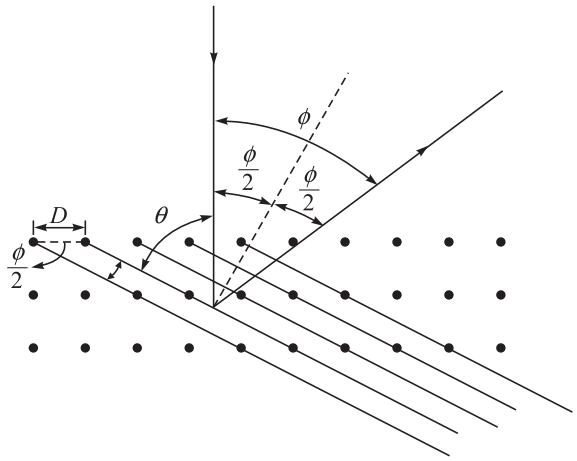


Figure 4.4 Diffraction of electron waves by a crystal.

The Bragg condition for constructive interference is

$$n\lambda = 2d \sin\theta$$

where d is the spacing between the adjacent Bragg planes and n is an integer. The angle θ is shown in the figure. We have

$$\theta + \phi + \theta = 180°$$

or

$$\theta = \frac{180^\circ - \phi}{2}$$
$$= 90° - (\phi/2)$$

From geometry,

$$d = D\sin\frac{\phi}{2}$$

where D is the interatomic spacing. Therefore,

$$n\lambda = 2D \sin\frac{\phi}{2} \sin\left(90° - \frac{\phi}{2}\right)$$
$$= 2D \sin\frac{\phi}{2} \cos\frac{\phi}{2}$$
$$= D \sin\phi$$

For nickel $D = 2.15$ Å. Assuming that the peak at $\phi = 50°$ corresponds to first order diffraction, we take $n = 1$. Therefore,

$$\lambda = 2.15 \times \sin 50°$$
$$= 1.65 \text{ Å}$$

Now, according to de Broglie's hypothesis, we have for electrons accelerated though a potential difference V (Equation 4.7),

$$\lambda = \frac{12.3}{\sqrt{V}} \text{ Å}$$
$$= \frac{12.3}{\sqrt{54}} = 1.66 \text{ Å}$$

The agreement between the two values is remarkably close.

The experiment was performed at various electron energies by varying the voltage V and in each case the two values of λ agreed. This also confirmed the variation of λ with the momentum of the electron as given by the de Broglie relation (4.1). Higher order diffraction maxima, corresponding to $n > 1$, were also observed and found to be in good agreement with de Broglie's hypothesis.

G.P. Thomson's Experiment

In this experiment, a beam of highly-accelerated electrons was directed towards a thin foil of some polycrystalline material. After passing through the foil, the electrons were received on a photographic plate. It was found that a diffraction pattern, consisting of a series of concentric rings, is formed on the plate (Figure 4.5). This pattern was similar to Debye-Scherrer X-ray diffraction pattern, confirming the wave nature of electrons.

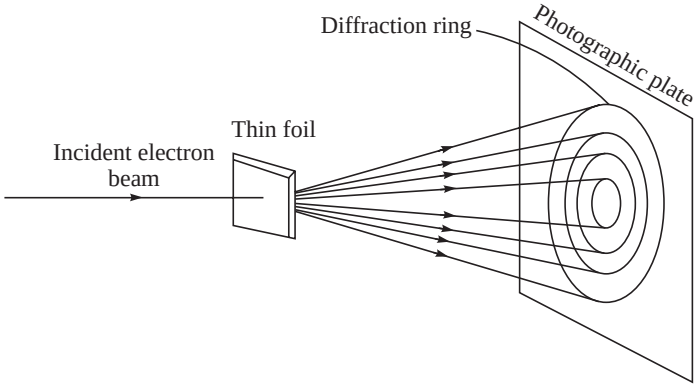


Figure 4.5 G.P. Thomson's experiment.

Thomson obtained the wavelength of the electrons from the de Broglie formula (4.7) and then calculated the spacing d between atomic planes using Bragg's equation. It was found that the value of d is same as that obtained from X-ray experiments.

Subsequently, various experiments were performed to obtain diffraction patterns for neutrons and certain atoms and molecules, showing the universality of matter waves and the de Broglie formula. Young's type double-slit interference patterns have also been obtained for electrons as discussed in the next section. De Broglie was awarded the 1929 Nobel Prize in physics and Davisson and Thomson shared the 1937 Nobel Prize*.

PROBLEM 4.10 In a Davisson-Germer diffraction experiment electrons of kinetic energy 100 eV are scattered from a crystal. The first maximum in intensity occurs at $\theta = 10.0°$. (a) What is the spacing between the crystal planes? (b) How many peaks will there be in the interference pattern?

Solution: (a) The Bragg condition for constructive interference is

$$n\lambda = 2d \sin \theta$$

For first maximum, $n = 1$. Therefore, the spacing between the crystal planes is

$$d = \frac{\lambda}{2\sin\theta}$$

The de Broglie wavelength λ is given by

$$\lambda = \frac{12.3}{\sqrt{V}} \text{Å} = \frac{12.3}{\sqrt{100}} \text{Å} = 1.23 \text{ Å}$$

Therefore,

$$d = \frac{1.23}{2 \times \sin 10°} = \frac{1.23}{2 \times 0.174}$$

$$= \boxed{3.53 \text{ Å}}$$

(b) Let the number of peaks in the interference pattern be n. Since the maximum possible value of $\sin \theta$ is 1, we have

$$n\lambda \leq 2d$$

or

$$n \leq \frac{2d}{\lambda} = \frac{2 \times 3.53}{1.23} = 5.74$$

Therefore, the largest possible value of n is 5.

Thus, the number of peaks = $\boxed{5}$

PROBLEM 4.11 A narrow beam of electrons, accelerated through a potential difference of 30 kV, passes through a thin aluminium foil and produces a diffraction pattern on a photographic plate on the opposite side of the foil. If the first diffraction ring is obtained at an angle of 59′ 36″ from the incident beam, calculate the grating space in the aluminium crystals.

* G.P. Thomson was son of J.J. Thomson. It is interesting to note that J.J. Thomson was given the Nobel Prize (in 1906) for showing that the electron has *particle* nature while G.P. Thomson was given the same prize for showing that the electron has *wave* nature.

Solution: As is clear from Figure 4.6, the glancing angle θ is related to the angle of deviation α by

$$\alpha = 2\theta$$

or
$$\theta = \frac{\alpha}{2} = \frac{59'36''}{2} = 29'48''$$

For the first order ring ($n = 1$),

$$2d \sin \theta = \lambda$$

or
$$d = \frac{\lambda}{2\sin\theta}$$

For electrons accelerated through a potential V volts

$$\lambda = \frac{12.3}{\sqrt{V}} \text{ Å}$$

Therefore,
$$d = \frac{12.3}{2 \times \sqrt{30{,}000} \times \sin 29'48''}$$

$$= \frac{12.3}{2 \times 173.2 \times 0.0087}$$

$$= \boxed{4.08 \text{ Å}}$$

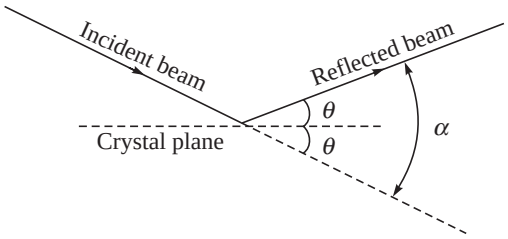


Figure 4.6

4.3 THE DOUBLE-SLIT EXPERIMENT WITH PARTICLES

In section 2.4 we pointed to the conceptual difficulty that arises when we try to analyze the double-slit interference experiment with a radiation source. We find that both the wave and particle aspects of radiation are exhibited in the same experiment. Thus, the double-slit experiment is an excellent way of demonstrating the *wave-particle duality* of radiation. A similar experiment can be performed using material particles instead of electromagnetic radiation. Such experiments have been performed with electrons by Möllenstedt and Dücker (1956), by Jönsson (1961) and more recently by Tonomura et al. (1989)[†].

[†] A. Tonomura et al., *American Journal of Physics*, **57**, 117 (1989).

Let a monoenergetic beam of electrons, emitted from a source *S* be incident on two slits *A* and *B* (Figure 4.7). The widths and spacing of the slits are chosen to be of the same order of magnitude as the de Broglie wavelength of the incident electrons. After passing through the slits, the electrons fall on the screen *P*. The screen incorporates an array of microscopic counters (*C*) which can record each electron striking the screen at any point. Or, the screen may be a fluorescent one, which can be photographed.

Figure 4.8 shows the intensity *I* (number of electrons arriving at a point in a given time) as a function of position *x* on the screen. If slit *B* is blocked, the pattern observed on the screen looks like that shown in Figure 4.8 (a). Similarly, if slit *A* is blocked, the pattern looks like that in Figure 4.8 (b). If the electrons behaved as classical particles, then, on opening both the slits, the expected pattern would be as shown in Figure 4.8 (c). However, when both the slits are open, the pattern is as shown in Figure 4.8 (d). This is clearly a double-slit interference pattern, exhibiting the wave behaviour of electrons.

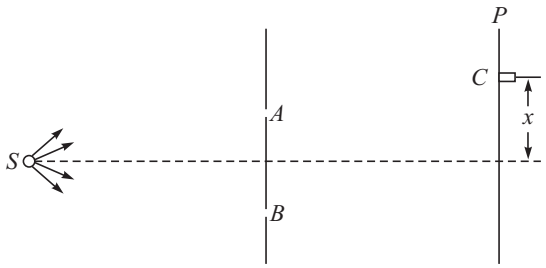


Figure 4.7 Double-slit experiment with electrons.

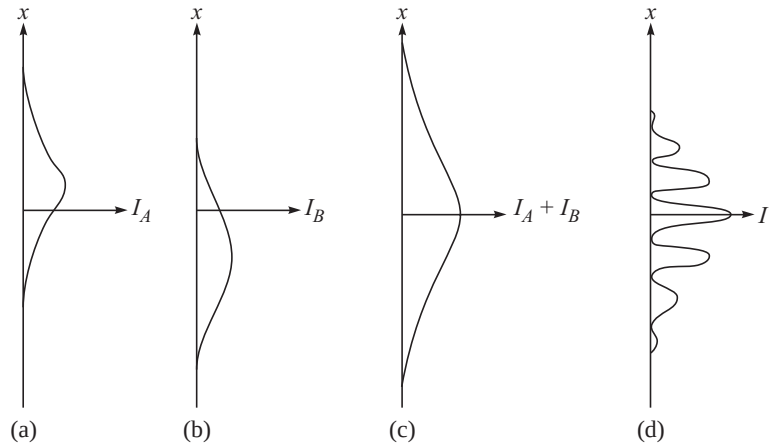


Figure 4.8 Variation of intensity (*I*) with the position on the screen (*x*).

We might at first be inclined to think that the pattern is due to the interference between electrons passing through the two slits. That this is not true was demonstrated by Tonomura et al. by reducing the incident electron

intensity to such a low level that only one electron was fired at a time towards the slits. The interference pattern was still produced after a large number of electrons were fired. This compels us to conclude that interference does not occur between different electrons, but is a property of a single electron. In other words, each electron interacts with both the slits and, as such, it is meaningless to ask which slit the electron passes through.

If we employ a detector that can tell which slit an electron goes through, the *interference pattern disappears*. Thus on detection, the electron exhibits particle-like properties—it is localized and is recorded by only one detector at a time. We see that both the wave and particle natures of electrons are exhibited in this experiment. We shall discuss more about the measurement process when we discuss Heisenberg's uncertainty principle.

4.4 THE NEED FOR A WAVE FUNCTION

The results of the double-slit experiment lead to the inevitable conclusion that each particle *interferes with itself* in some way. The crucial question that arises, therefore, is: How do we describe a particle interfering with itself and thus reaching the screen so as to fall in a certain interference pattern?

The clue comes from the classical theory of waves. We know that waves are characterized by an amplitude function such that the intensity of the wave at any point is determined by the square of the amplitude. Following this, it is assume that associated with each particle is a wave function $\Psi(x, t)$ such that the absolute square of this function gives the intensity I:

$$I = |\Psi(x, t)|^2 = \Psi^*(x, t)\, \Psi(x, t) \tag{4.11}$$

where * denotes complex-conjugation. For simplicity, we have taken one-dimensional wave function but the treatment can be easily generalized to three dimensions. Absolute value of Ψ is taken because, as we shall see later, the wave function is, in general, a complex quantity. The intensity, on the other hand, is a real, positive quantity.

Now, in Young's double-slit experiment with light, the intensity at a point on the screen is given by the square of the amplitude of the wave formed by the superposition of the secondary waves arising from the two slits. In the case of the double-slit experiment with particles, let Ψ_1 be the wave function at some point on the screen corresponding to the waves spreading from slit 1 and Ψ_2 be the wave function at the same point corresponding to the waves spreading from slit 2. The corresponding intensities on the screen when only one slit is open are

$$I_1 = |\Psi_1|^2 \quad \text{and} \quad I_2 = |\Psi_2|^2 \tag{4.12}$$

When both the slits are open, the two amplitudes Ψ_1 and Ψ_2 superpose to give the resultant amplitude:

$$\Psi = \Psi_1 + \Psi_2 \tag{4.13}$$

The resultant intensity is, therefore

$$I = |\Psi|^2 = |\Psi_1 + \Psi_2|^2 \tag{4.14}$$

Let us write

$$\Psi_1 = |\Psi_1|e^{i\alpha_1},\ \Psi_2 = |\Psi_2|e^{i\alpha_2} \tag{4.15}$$

where $|\Psi_1|$, $|\Psi_2|$ are the absolute values and α_1, α_2 are the phases of the two wave functions, respectively. Then

$$|\Psi_1|^2 = \Psi_1^*\,\Psi_1 \quad \text{and} \quad |\Psi_2|^2 = \Psi_2^*\Psi_2 \tag{4.16}$$

This gives

$$\begin{aligned} I &= (\Psi_1 + \Psi_2)^*\,(\Psi_1 + \Psi_2) \\ &= \Psi_1^*\Psi_1 + \Psi_2^*\Psi_1 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_2 \\ &= |\Psi_1|^2 + |\Psi_2|^2 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_1 \\ &= |\Psi_1|^2 + |\Psi_2|^2 + |\Psi_1|\,|\Psi_2|\,(e^{-i(\alpha_1 - \alpha_2)} + e^{i(\alpha_1 - \alpha_2)}) \\ &= I_1 + I_2 + 2\sqrt{I_1 I_2}\,\cos(\alpha_1 - \alpha_2) \end{aligned} \tag{4.17}$$

This shows that $I \neq I_1 + I_2$, in keeping with the observation of section 4.3 (see Figure 4.8). The last term in Equation (4.17) is the *interference* term. It depends on the relative phase $(\alpha_1 - \alpha_2)$ of Ψ_1 and Ψ_2. As the two phases α_1 and α_2 vary with position, an interference pattern is formed on the screen.

We shall see in chapter 6 that the wave function satisfies a *linear equation* which is known as the *Schrödinger equation*. The linearity implies that if Ψ_1 and Ψ_2 are any two solutions of the equation, then $\Psi_1 + \Psi_2$ is also a solution. This is necessary for the superposition principle (Equation 4.13) to be valid.

4.5 BORN'S INTERPRETATION OF THE WAVE FUNCTION

It must be apparent to the reader that, unlike classical waves such as electromagnetic waves or sound waves, the quantum mechanical wave function $\Psi(x, t)$ is an *abstract quantity*. This was realized by Max Born, who in 1926, suggested that the wave function must be interpreted statistically. **Born's postulate** can be stated as follows:

If a particle is described by a wave function $\Psi(x, t)$, then the *probability* $P(x)\,dx$ of finding the particle within an element dx about the point x at time t is

$$\boxed{P(x)\,dx = |\Psi(x,t)|^2\,dx} \tag{4.18}$$

The quantity

$$P(x) = |\Psi(x,\ t)|^2 = \Psi^*(x,\ t)\Psi(x,\ t) \tag{4.19}$$

is, naturally, called the **position probability density**.

Since the probability of finding the particle somewhere must be unity, the wave function should be *normalized* so that

$$\boxed{\int_{-\infty}^{\infty} \Psi^*\Psi\,dx = 1} \tag{4.20}$$

That is, the wave function should be *square integrable.*

The probabilistic interpretation of the wave function has to be justified by the success of the theory that is built on it. However, the interpretation seems to be quite consistent with the earlier observation related to interference of electrons in the double-slit experiment. The wave function Ψ produces the interference pattern. At places where $|\Psi|^2$ is large, the probability of a particle arriving there is large. Therefore, the particles reaching the screen distribute themselves in the pattern dictated by the probability density function $|\Psi|^2$.

The genius of Born was acknowledged by the scientific community very late. He was awarded the Nobel prize in 1954 for the great work that the did in 1926 for the development of quantum mechanics.

SUMMARY

1. In 1924, de Broglie postulated that with every material particle a wave is associated, having wavelength

$$\lambda = \frac{h}{p}$$

where p is the momentum of the particle and h is Planck's constant.

2. de Broglie's hypothesis was experimentally verified in 1927 by Davisson and Germer and independently by G.P. Thomson by demonstrating that electrons were diffracted by crystals in a manner similar to X-rays.

3. The double-slit experiments carried out using beams of material particles (electrons, neutrons etc.) exhibit interference patterns similar to those obtained with light. It was found that interference does not occur between different particles but is a property of a single particle. That is, each particle interferes with itself.

4. In order to explain the interference effects, it is assumed that with each particle a wave function is associated. Born postulated that if a particle is described by a wave function $\Psi(x, t)$, then $|\Psi(x, t)|^2\ dx$ gives the probability of finding the particle within an element dx about the point x at time t. Since the probability of finding the particle somewhere must be unity, the wave function must be normalized:

$$\int_{-\infty}^{\infty} \Psi^* \Psi\, dx = 1$$

QUESTIONS

1. State de Broglie's hypothesis. Derive the expressions for the de Broglie wavelength of a particle in terms of (a) its kinetic energy, (b) accelerating potential, both for the nonrelativistic and the relativistic cases.

2. Describe the Davisson-Germer experiment for establishing the wave nature of electrons.

3. Describe G.P. Thomson's experiment for establishing the wave nature of electrons.
4. Briefly describe the results of the double-slit experiment with electrons. What conclusion is drawn from it? Discuss how the association of a wave function with the electron explains the interference effects.
5. What is Born's interpretation of the wave function associated with a particle?

EXERCISES

1. Calculate the de Broglie wavelength associated with a proton moving with a speed equal to one-twentieth of the speed of light.
   Mass of proton = 1.67×10^{-27} kg, $h = 6.6 \times 10^{-34}$ Js.
   [***Ans.*** 2.63×10^{-14} m]
2. Calculate the de Broglie wavelength of a neutron having kinetic energy 28.8 eV. Given: mass of neutron = 1.67×10^{-27} kg, $h = 6.62 \times 10^{-34}$ Js.
   [***Ans.*** 4.2 Å]
3. What voltage must be applied to an electron microscope to produce electrons of wavelength 0.50 Å? Mass of electron = 9.0×10^{-31} kg.
   [***Ans.*** 602.4 V]
4. Calculate the de Broglie wavelength of an alpha particle accelerated through a potential difference of 2000 V. [***Ans.*** 2.3×10^{-3} Å]
5. A nonrelativistic electron has wavelength 2.0 Å. What is its energy?
   [***Ans.*** 37.5 eV]
6. Find the velocity of an electron if its de Broglie wavelength is 1.2 Å.
   [***Ans.*** 6.0×10^{6} m/s]
7. A narrow electron beam, accelerated through a potential difference of 10 kV, is passed through a thin film of a metal for which the spacing of the atomic planes is 55 pm. What is the angle of deviation of the first order diffraction maximum? [***Ans.*** 12°44′]
   [**Hint.** The angle of deviation is twice the glancing angle θ in Bragg's formula.]

Chapter

Wave Packets and the Uncertainty Principle

5

Chapter Contents

5.1 Representation of a Particle by a Wave Packet
5.2 Heisenberg's Uncertainty Principle
5.3 Illustrations of the Uncertainty Principle
5.4 Applications/Consequences of the Uncertainty Principle

5.1 REPRESENTATION OF A PARTICLE BY A WAVE PACKET

In chapter 4, we found that material particles exhibit wave nature and, therefore, a wave function must be associated with each particle. The momentum p of a particle and the wavelength λ of the wave associated with it are connected by the de Broglie relation

$$p = \frac{h}{\lambda} = \hbar k \tag{5.1}$$

where $k = 2\pi/\lambda$ is called the *propagation constant* or the *wave number*. Further, the energy E of the particle and the frequency ν of the associated wave are connected by the Planck-Einstein relation

$$E = h\nu = \hbar\omega \tag{5.2}$$

where $\omega = 2\pi\nu$ is the *angular frequency* of the wave.

As a first step towards constructing a wave function to be associated with a particle, let us consider a plane, monochromatic wave

$$\Psi(x, t) = Ae^{i(kx-\omega t)} \tag{5.3}$$

which represents a simple harmonic disturbance of wavelength $\lambda = 2\pi/k$ and frequency $\nu = \omega/2\pi$, travelling towards the positive x-direction with velocity

$$v_{\text{ph}} = \frac{\omega}{k} \tag{5.4}$$

The subscript "ph" indicates that this velocity is called *phase velocity*. For simplicity, we shall restrict the discussion to one dimension though it can be easily generalized to three dimensions.

The plane wave (5.3) represents a particle having a definite momentum $p = \hbar k$. However, since its amplitude A is constant, it corresponds to a complete lack of localization of the particle in space. Indeed, the *probability density* (see Equation 4.19)

$$P = |\Psi(x, t)|^2 = A^2 \tag{5.5}$$

is independent of position. Thus, the particle has equal probability of being found anywhere from minus to plus infinity. Clearly, a single plane wave cannot represent a localized particle.

So, the question that arises is: how to construct a wave function that can look like a particle? If a wave is to be associated with a particle, then its amplitude should be sizeable in the neighborhood of the particle and negligible elsewhere. This suggests that a particle can be represented by a wave packet. *A wave packet can be formed by superposing plane waves of different wave numbers in such a way that they interfere with each other destructively outside of a given region of space.* The mathematical technique for doing this is that of Fourier integral and transforms, which is summarized in Appendix A.

Let $\Psi(x, t)$ be a one-dimensional wave packet formed by superposition of plane waves:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega t)}\, dk \tag{5.6}$$

where the amplitude A and the angular frequency ω depend on k. It is clear that in order to represent a free particle by a wave packet, we must give up the requirement that the particle should have a precisely defined momentum. The factor $1/\sqrt{2\pi}$ has been chosen for later convenience.

The amplitude function $A(k)$ is obtained by taking the inverse Fourier transform of $\Psi(x, t)$:

$$A(k) e^{-i\omega t} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t)\, e^{-ikx}\, dx$$

or

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t)\, e^{-i(kx - \omega t)}\, dx \tag{5.7}$$

Since we want the wave packet to describe a particle, we must now *localize* it. For this, we assume that $A(k)$ is centred about some particular value $k = k_0$,

falling rapidly to zero outside an interval $\left(k_0 - \frac{\Delta k}{2}, k_0 + \frac{\Delta k}{2}\right)$, where Δk is small. Then,

$$\Psi(x,\ t) = \frac{1}{\sqrt{2\pi}} \int_{k_0 - \frac{\Delta k}{2}}^{k_0 + \frac{\Delta k}{2}} A(k)\ e^{i(kx - \omega t)}\, dk \tag{5.8}$$

We assume further that ω varies slowly with k, so that we may expand it in a Taylor series about k_0:

$$\omega(k) = \omega(k_0) + (k - k_0)\left(\frac{d\omega}{dk}\right)_{k=k_0} + \frac{1}{2}(k - k_0)^2\left(\frac{d^2\omega}{dk^2}\right)_{k=k_0} + \ldots$$

Neglecting second and higher order terms because we are considering values of k close to k_0, and putting $\omega(k_0) = \omega_0$, we obtain

$$\Psi(x,\ t) = \frac{1}{\sqrt{2\pi}} \int_{\Delta k} A(k)\ \exp\left[i\left\{(k - k_0)x + k_0 x - \omega_0 t - (k - k_0)t\frac{d\omega}{dk}\right\}\right] dk$$

$$= f(x,\ t)e^{i(k_0 x - \omega_0 t)} \tag{5.9}$$

where

$$f(x,\ t) = \frac{1}{\sqrt{2\pi}} \int_{\Delta k} A(k)\exp\left[i\left(x - \frac{d\omega}{dk}t\right)(k - k_0)\right] dk \tag{5.10}$$

Equation (5.9) shows that the wave function $\Psi(x, t)$ is a wave of wavelength $2\pi/k_0$ and frequency $\omega_0/2\pi$ modulated by the envelope $f(x, t)$. The envelope depends upon x and t only through the combination $x - (d\omega/dk)\, t$. Thus, it represents a **wave packet** which moves with the *group velocity*

$$\boxed{v_g = \frac{d\omega}{dk}} \tag{5.11}$$

Figure 5.1 shows the schematic diagram of a wave packet propagating along the x-axis.

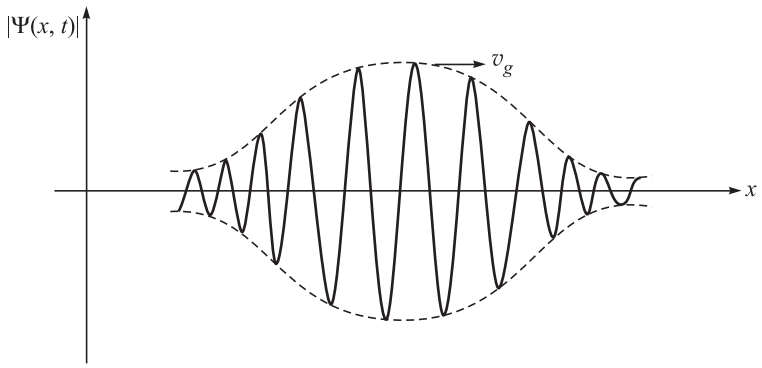


Figure 5.1 A wave packet propagating along the x-axis.

Before proceeding further, we point out one interesting and important general property of wave packets. If Δx is the spatial extent of a wave packet and Δk is its wave number range, then it always happens that

$$\boxed{\Delta x\, \Delta k \geq 1} \tag{5.12}$$

Thus, it is impossible to make both the "widths" Δx and Δk small. The smaller the spatial extent of a wave packet, the larger is the range of wave numbers in its Fourier decomposition, and vice versa. This general feature of wave packets has very deep implications in quantum mechanics in the form of *Heisenberg's uncertainty principle* as we shall see in section 5.2.

An example illustrating the **reciprocity relation** (5.12) is given in Problem 5.1.

Let us now use the relations (5.1) and (5.2) to link wave packets with material particles. We write

$$v_g = \frac{d(\hbar\omega)}{d(\hbar k)} = \frac{dE}{dp} \tag{5.13}$$

This is the familiar classical Hamiltonian expression for the velocity of a particle. For a nonrelativistic free particle of mass m,

$$E = \frac{p^2}{2m}$$

Therefore,
$$\frac{dE}{dp} = \frac{p}{m} = \frac{mv}{m} = v \tag{5.14}$$

where v is the velocity of the particle.

In the relativistic case,

$$E^2 = p^2c^2 + m^2c^4$$

or
$$2E\,\frac{dE}{dp} = 2pc^2$$

or
$$\frac{dE}{dp} = \frac{pc^2}{E}$$

Now,
$$E = \gamma mc^2 \quad \text{and} \quad p = \gamma mv$$

where
$$\gamma = 1\Big/\sqrt{1 - v^2/c^2}$$

Therefore,
$$v_g = \frac{dE}{dp} = \frac{\gamma mv\,c^2}{\gamma mc^2} = v \tag{5.15}$$

Thus, both for a relativistic and a nonrelativistic particle, the group velocity of the associated wave packet is to be identified with the velocity of the particle.

Let us look at the phase velocity in the two cases. For a nonrelativistic particle,

$$v_{\text{ph}} = \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{E}{p} = \left(\frac{p^2}{2m}\right)\frac{1}{p} = \frac{p}{2m} = \frac{v}{2} \tag{5.16}$$

On the other hand, for a relativistic particle

$$v_{\text{ph}} = \frac{E}{p} = \frac{\gamma mc^2}{\gamma mv} = \frac{c^2}{v} \tag{5.17}$$

Thus, in the first case v_{ph} is less than the speed of the particle and in the second case it is more than the speed of light. Clearly, the phase velocity has no physical significance.

The wave function $\Psi(x, t)$ can now be written as

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p)\ e^{(i/\hbar)(px-Et)}\ dp \tag{5.18}$$

where $A(k)$ has been replaced by the *momentum amplitude function* $\phi(p)$. If we define

$$\Phi(p, t) = \phi(p)\, e^{-iEt/\hbar} \tag{5.19}$$

then (5.18) becomes

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p, t) e^{ipx/\hbar}\, dp \tag{5.20}$$

and, taking the inverse Fourier transform of $\Psi(x, t)$

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t)\, e^{-ipx/\hbar}\, dx \tag{5.21}$$

At time $t = 0$,

$$\psi(x) = \Psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar}\, dx \tag{5.22}$$

and

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x)\, e^{-ipx/\hbar}\, dx \tag{5.23}$$

$\Phi(p, t)$ (or $\phi(p)$) is called the **wave function in momentum space.**

It can be shown that

$$\boxed{\int_{-\infty}^{\infty} |\Phi(p, t)|^2\, dp = \int_{-\infty}^{\infty} |\Psi(x, t)|^2\, dx = \text{constant}} \tag{5.24}$$

This result is called **Parseval's theorem.** It shows that if $\Psi(x, t)$ is normalized to unity then so is $\Phi(p, t)$.

Wave Packets in Three Dimensions

The above discussion of one-dimensional wave packets can be easily extended to three dimensions. The three-dimensional wave packet is

$$\Psi(\mathbf{r}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} \Phi(\mathbf{p}, t)\, e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\, d\mathbf{p} \tag{5.25}$$

where $d\mathbf{p} = dp_x\, dp_y\, dp_z$ is the volume element in momentum space. Taking inverse transform,

$$\Phi(\mathbf{p}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int_{-\infty}^{\infty} \Psi(\mathbf{r}, t)\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\, d\mathbf{r} \tag{5.26}$$

where $d\mathbf{r} = dx\, dy\, dz$ is the volume element in coordinate space.

Parseval's theorem is

$$\int |\Psi(\mathbf{r}, t)|^2\, d\mathbf{r} = \int |\Phi(\mathbf{p}, t)^2 d\mathbf{p} \tag{5.27}$$

PROBLEM 5.1 A wave packet has the amplitude function

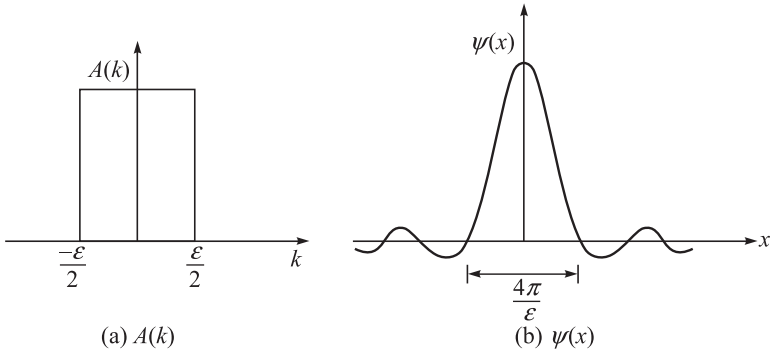
$$A(k) = \begin{cases} 1/\sqrt{\varepsilon}, & -\varepsilon/2 \le k \le \varepsilon/2 \\ 0, & |k| > \varepsilon/2 \end{cases}$$

Find the wave function $\psi(x)$ and hence verify the reciprocity relation $\Delta x\, \Delta k > 1$.

Solution: $\psi(x)$ is obtained by taking the Fourier transform of $A(k)$:

$$\begin{aligned} \psi(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k)\, e^{ikx}\, dk \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\varepsilon/2}^{\varepsilon/2} \frac{1}{\sqrt{\varepsilon}} e^{ikx}\, dk \\ &= \frac{1}{\sqrt{2\pi\varepsilon}} \left[\frac{e^{ikx}}{ix} \right]_{-\varepsilon/2}^{\varepsilon/2} \\ &= \frac{1}{\sqrt{2\pi\varepsilon}} \frac{2}{x} \frac{e^{i\varepsilon x/2} - e^{-i\varepsilon x/2}}{2i} \\ &= \sqrt{\frac{2}{\pi\varepsilon}} \frac{\sin(\varepsilon x/2)}{x} \end{aligned}$$

The graphs of $A(k)$ and $\psi(x)$ are shown in Figure 5.2. The central peak of $\psi(x)$ falls to zero at $x = \pm 2\pi/\varepsilon$. Therefore, the width of $\psi(x)$ is



(a) $A(k)$ (b) $\psi(x)$

Figure 5.2 A function and its Fourier transform.

$$\Delta x = 4\pi/\varepsilon$$

The width of $A(k)$ is

$$\Delta k = \varepsilon$$

Therefore, $$\Delta x\, \Delta k = 4\pi$$

Thus, the reciprocity relation is verified.

5.2 HEISENBERG'S UNCERTAINTY PRINCIPLE

In classical mechanics, the position and the momentum of a particle are independent of each other and can be simultaneously measured precisely. In quantum mechanics, a particle is represented by a wave packet. The particle may be found anywhere within the region where the amplitude of the wave function $\psi(x)$ is nonzero. Thus, the position of the particle is indeterminate within the width of the wave packet. Similarly, the momentum of the particle is indeterminate within the region where the momentum wave function $\phi(p)$ is nonzero. An important question that arises is: How precisely we can determine the position and the momentum of a particle simultaneously? In order to answer this question, we recall the reciprocity relation (5.12) between the widths in the x-space and k-space wave functions:

$$\Delta x \Delta k \geq 1$$

Using the relation $\hbar k = p$, we obtain

$$\boxed{\Delta x\, \Delta p \geq \hbar} \tag{5.28}$$

This is **Heisenberg's uncertainty relation for position and momentum**. It states that *it is not possible to specify both the position and the momentum of a particle simultaneously with arbitrary precision; the product of the uncertainties in the position and the momentum is always greater than a quantity of order* $\hbar$.

In chapter 6, we shall obtain the exact statement of the uncertainty relation as

$$\Delta x \Delta p \geq \hbar/2 \tag{5.28a}$$

The relation (5.28) can be easily generalized to three dimensions:

$$\boxed{\begin{aligned} \Delta x\, \Delta p_x &\geq \hbar \\ \Delta y\, \Delta p_y &\geq \hbar \\ \Delta z\, \Delta p_z &\geq \hbar \end{aligned}} \tag{5.29}$$

It is important to note that there is no uncertainty relation between one cartesian component of the position vector of a particle and a different cartesian

component of the momentum. The restrictions are only on the complementary pairs: Δx, Δp_x; Δy, Δp_y and Δz, Δp_z.

It is also important to note that the uncertainty relation does not place any restriction on the precision with which a position or a momentum measurement of a particle can be made. But once the system is known to have one of these quantities defined to within a precision ε, then the measurements of the other quantity subsequently will give values spread over a range $\geq \hbar/\varepsilon$. Thus, more precisely one of the quantities is known, the greater is the range of values that will be obtained in a series of measurements of the other quantity.

Energy-Time Uncertainty Relation

The position-momentum uncertainty relation can be used to obtain another uncertainty relation—the one involving energy and time. The energy E of a free particle of mass m and momentum p is

$$E = \frac{p^2}{2m}$$

If Δp is the uncertainty in momentum then the uncertainty in energy is

$$\Delta E = \frac{2p}{2m}\ \Delta p = \frac{p}{m}\ \Delta p = v\,\Delta p$$

where v is the velocity of the particle.

If the spatial width of the wave packet representing the particle is Δx, then the time required for the packet to pass a given point, and hence the uncertainty in its localizability in time, is

$$\Delta t = \frac{\Delta x}{v}$$

Multiplying the two,

$$\Delta E\ \Delta t = (v\Delta p)\left(\frac{\Delta x}{v}\right) = \Delta x\ \Delta p \geq \hbar$$

or

$$\Delta E \Delta t \geq \hbar \tag{5.30}$$

This relation may also be deduced directly from the form of the wave packet (5.18) since E and t appear in the same reciprocal relation as p and x. A wave packet of duration Δt must be composed of plane-wave components whose energies extend over a range ΔE such that (5.30) is satisfied. Thus, this relation connects the uncertainty ΔE in the determination of the energy of a system with the time interval Δt available for the energy determination. In the context of quantum mechanics, it implies that a state of finite duration cannot have a precisely defined energy. Thus, if an excited atomic or nuclear state has a life time τ, its energy is uncertain by an amount at least of order $\hbar/\tau$. For the energy of a quantum state to be precisely defined, it must have infinite life time.

General Statement of the Uncertainty Principle

The uncertainty relations (5.29) and (5.30) are obtained as a mathematical property of wave packets. They are forced on us by the need to reconcile the wave-particle duality of matter. These relations are particular examples of the uncertainty principle, formulated by Heisenberg in 1927. He recognized it as a basic principle that underlies the structure of quantum mechanics. The principle can be stated as:

The Uncertainty Principle

It is impossible to simultaneously specify the precise values of both members of certain pairs of dynamical variables of a system. These variables, called *complementary variables*, are canonically conjugate to each other in the classical Hamiltonian sense. The product of the uncertainties in the values of the two variables is at least of the order of $\hbar$.

The most common examples of complementary variable are: A cartesian coordinate of a particle and the corresponding component of momentum (x, p_x; y, p_y; z, p_z), a component of angular momentum of a particle and its angular position in a perpendicular plane (e.g. J_z, ϕ), the energy E of a particle and the time t at which it is measured. There is no complementarity between one cartesian coordinate of a particle and a different momentum component (e.g. x and p_y).

It must be kept in mind that the limitations on measurement imposed by the uncertainty principle have nothing to do with the experimental errors that occur in actual measurements. Further, the smallness of $\hbar$ ensures that the uncertainty principle is relevant only for systems of atomic dimensions. No results of classical mechanics are affected for macroscopic bodies.

The uncertainty principle is valid for photons as well as for material particles.

5.3 ILLUSTRATIONS OF THE UNCERTAINTY PRINCIPLE

We now describe some experiments which help up to understand more clearly how the process of measurement creates uncertainties which are in accordance with Heisenberg's uncertainty principle and are forced on us by the need to reconcile the wave and particle aspects of matter and radiation.

Heisenberg's Gamma-ray Microscope

This is an idealized "thought" (*gedanken*) experiment devised by Heisenberg himself. A thought experiment is an imaginary experiment which is consistent with the laws of physics but is not possible to carry out in actual practice. Such experiments are frequently used in physics to clarify difficult concepts in a simple manner.

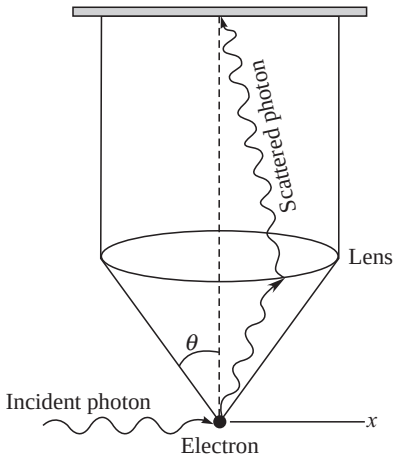


Figure 5.3 Gamma-ray microscope.

This experiment attempts to determine the position of an electron by observing it through a microscope (Figure 5.3). The initial momentum of the electron is known precisely. For simplicity, we assume it to be at rest initially. In order to observe the electron, it must be illuminated by radiation which is scattered by the electron into the microscope. If λ is the wavelength of the scattered radiation, then the x-component of the electron position cannot be determined to a precision greater than the limit of resolution of the microscope, which is given by

$$\Delta x \approx \frac{\lambda}{2\sin\theta} \tag{5.31}$$

where θ is the half-angle subtended by the lens at the electron position. This is the uncertainty in the position of the electron. Clearly, smaller the wavelength of the illuminating radiation, smaller will be the uncertainty in position measurement. Therefore, one must employ light of shortest possible wavelength. Hence the name γ-ray microscope, because γ-rays have the shortest wavelengths. Δx can also be decreased by increasing θ (for example, by making the lens aperture larger).

Now, in order that the electron be observed, at least one of the incident photons must be scattered by the electron into the microscope. This Compton scattering imparts to the electron a recoil momentum which is of the order of magnitude of the photon momentum h/λ. However, the direction in which the photon is scattered cannot be known exactly because it can be scattered anywhere within the aperture of the lens. From the figure, the x-component of the momentum of the scattered photon ranges from $-\frac{h}{\lambda}\sin\theta$ to $+\frac{h}{\lambda}\sin\theta$. Therefore, the uncertainty in the x-component of the recoil momentum is

$$\Delta p_x \approx 2\left(\frac{h}{\lambda}\sin\theta\right) \tag{5.32}$$

Note that Δp_x can be reduced by increasing λ and/or decreasing θ, but both these steps would increase Δx. Multiplying (5.31) and (5.32), we get

$$\Delta x \, \Delta p_x \approx h$$

which is in accordance with the uncertainty principle. Thus, our idealized thought experiment does not allow us to escape the requirements of the uncertainty principle.

Single-Slit Diffraction Experiment

Suppose a beam of electrons (or some other particles including photons) is moving along the x-direction with a well-defined momentum p. If this beam is made to pass through a slit of width a, as shown in the figure, then the y coordinate of the position of an electron passing through the slit is determined to an accuracy

$$\Delta y = a$$

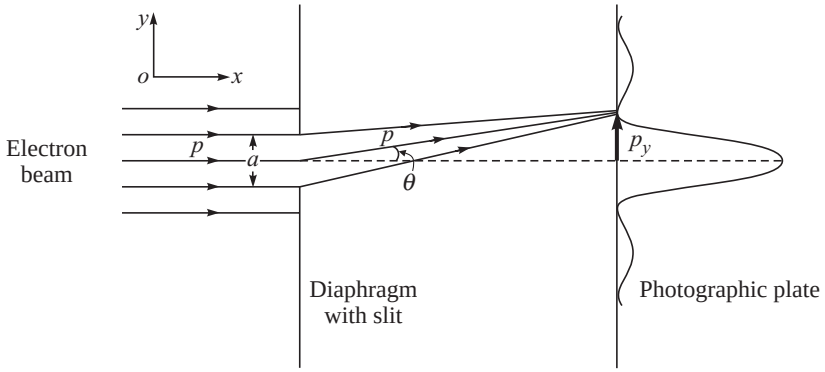


Figure 5.4 Single-slit diffraction.

Smaller the width of the slit, greater is the accuracy in the knowledge of the y coordinate of the electron at the instant it passes through the slit.

The electron has a wave associated with it, having de Broglie wavelength $\lambda = h/p$. Therefore, a diffraction pattern is observed on the photographic plate placed on the other side of the slit. Due to diffraction, the beam diverges and, as a result, an electron acquires a momentum component parallel to the slit, i.e., in the y-direction. Since the electron is most likely to be found within the central peak of the diffraction pattern, the uncertainty in the knowledge of the y component of the momentum of the electron is

$$\Delta p_y \approx p \sin \theta$$

where θ is the angular deviation corresponding to the first minimum.

Now, from the theory of diffraction,

$$\sin\,\theta = \frac{\lambda}{a}$$

Therefore, $$\Delta p_y \approx p \sin\,\theta = \frac{p\lambda}{a}$$

Clearly, a better knowledge of the y coordinate (that is, smaller a) results in lesser accuracy in the knowledge of the y component of momentum.

Combining the above equations, and putting $p = h/\lambda$, we get

$$\Delta y \Delta p_y \approx (a)\left(\frac{h}{\lambda}\right)\left(\frac{\lambda}{a}\right)$$

or $$\Delta y \Delta p_y \approx h$$

as required by the uncertainty principle.

Double-Slit Interference Experiment

Let us now return to the double-slit experiment with electrons (or any other particles including photons) discussed in section 4.3. It was mentioned therein that if we employ a detector that can tell which slit an electron goes through, the interference pattern disappears. We shall now see that the uncertainty principle ensures that this is exactly the case.

Figure 5.5 shows a schematic diagram of the double-slit experiment. The distance between the slits A and B is d and the distance between the slits and the screen is D.

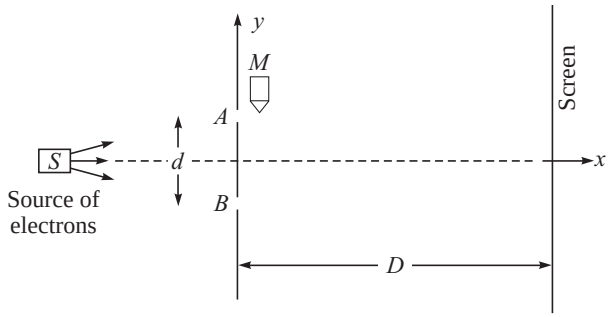


Figure 5.5 Double-slit experiment with a detector.

The distance between successive maxima on the screen would be

$$\beta = \frac{\lambda D}{d} \tag{5.33}$$

where λ is the de Broglie wavelength of the electron, that is,

$$\lambda = \frac{h}{p}$$

p being the momentum of the electron.

The detector is placed just behind the slits. It is a microscope along with a illumination device. In order that the microscope tells which slit the electron came through, it should measure the *y*-component of the electron's position to a precision better than half the distance between the slits. That is

$$\Delta y < \frac{d}{2} \tag{5.34}$$

In order to detect the electron, an illumination photon must bounce off the electron into the microscope. This will impart to the electron a momentum in the *y*-direction and thereby introduce an uncertainty Δp_y in the *y*-component of the electron's momentum. According to the uncertainty principle

$$\Delta p_y \geq \frac{\hbar}{\Delta y}$$

Using (5.34),

$$\Delta p_y \geq \frac{2\hbar}{d}$$

As a consequence, the direction of motion of the electron becomes uncertain by an angle $\Delta\theta$ given by

$$\Delta\theta \approx \frac{\Delta p_y}{p} \geq \frac{2\hbar}{d\,(h/\lambda)} = \frac{\lambda}{\pi d}$$

This angular uncertainty produces an uncertainty in the position of the electron on the screen given by

$$\Delta y = D\Delta\theta \geq \frac{\lambda D}{\pi d}$$

This is comparable with β, the distance between successive maxima of the interference pattern (see Equation 5.33). Thus, the uncertainty principle leads to the conclusion that if an attempt is made to determine through which slit the electron passes, the interference pattern disappears. Since this is known to be correct experimentally, the uncertainty principle must be true.

5.4 APPLICATIONS/CONSEQUENCES OF THE UNCERTAINTY PRINCIPLE

Since the Planck's constant is very small (6.63×10^{-34} Js), the uncertainty principle has significant consequences only for the microscopic systems. There are various phenomena in atomic and subatomic systems which can be understood in terms of this principle. It can also be used to make rough numerical estimates of various quantities connected with these systems. We discuss a few cases below.

The Ground State Energy and the Radius of the Hydrogen Atom

The position-momentum uncertainty relation can be used to obtain an estimate of the energy and the radius of an atom in its ground state. Let us discuss the simplest atom, hydrogen, which consists of a proton and an electron. If we assume the proton to be infinitely heavy, and hence at rest, the total classical energy of the electron is given by

$$E = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$$

where r is the radius of the electronic orbit. Classically, r can be made arbitrarily small and so there is no lower limit to the value of E. The uncertainty principle ensures that this is not possible in quantum mechanics. Since the linear size of the atom is of order r, the uncertainty in the position of the electron is

$$\Delta r \approx r$$

According to the uncertainty principle,

$$p \approx \Delta p \approx \hbar / r$$

Therefore,

$$E = \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\varepsilon_0 r} \tag{5.35}$$

The system will be in the state of lowest energy at the value of r given by

$$\frac{dE}{dr} = 0$$

or $$-\frac{\hbar^2}{mr^3} + \frac{e^2}{4\pi\varepsilon_0 r^2} = 0$$

or $$r = \frac{(4\pi\varepsilon_0)\hbar^2}{me^2}$$

This is same as the expression obtained for the first Bohr radius a_0 (see Equation 3.16). Its value is

$$r = a_0 = 0.53 \text{ Å}$$

Substituting in (5.35), the ground state energy of the hydrogen atom is

$$E = -\frac{me^4}{2\hbar^2 (4\pi\varepsilon_0)^2} = -\frac{\hbar^2}{2ma_0^2}$$

which is same as the Bohr's expression (see Equation 3.18). Its value is

$$E = -13.6 \text{ eV}$$

It is interesting to note that a qualitative discussion using the uncertainty principle leads to the correct ground-state energy and radius of the hydrogen atom. The precise agreement should not be taken too seriously. The important point to note is that the total energy of an atom has a minimum value which is compatible with the uncertainty principle. It is also clear why atoms are stable and do not collapse. To quote from **The Feynman Lectures on Physics**[†]:

So we now understand why we do not fall through the floor. As we walk, our shoes with their mass of atoms push against the floor with its mass of atoms. In order to squash the atoms close together, the electrons would be confined to a smaller space, and by the uncertainty principle, their momenta would have to be higher on the average, and that means high energy; the resistance to atomic compression is a quantum mechanical effect and not a classical effect.

Nonexistence of Electrons Inside the Nucleus

As we know, the size of a nucleus is of the order of 10^{-14} m. Therefore, for an electron to be confined within a nucleus, the uncertainty in its position should not exceed this value. The corresponding uncertainty in the momentum of the electron would be

$$\Delta p \geq \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{10^{-14}} = 1.1 \times 10^{-20} \text{ kg m/s}$$

The momentum p must be at least equal to Δp. An electron having such a large momentum has kinetic energy K much greater than its rest-mass energy m_0c^2. As such we may use the relativistic formula

$$\begin{aligned} K &\approx pc \\ &= 1.1 \times 10^{-20} \times 3 \times 10^8 \\ &= 3.3 \times 10^{-12} \text{ J} \\ &= \frac{3.3 \times 10^{-12}}{1.6 \times 10^{-13}} \text{ MeV} \\ &= 20.6 \text{ MeV} \end{aligned}$$

Experiments show that the electrons emitted from nuclei in β-decay have mostly energies between 2–3 MeV. From this we conclude that electrons cannot be basic constituents of nuclei. In fact, β-decay occurs when a neutron inside the nucleus transforms into a proton, an electron and a neutrino. The electron and the neutrino are immediately ejected out of the nucleus.

Let us see how much energy an electron must possess to be confined in an atom, say hydrogen. We have

$$\Delta x \approx 5 \times 10^{-11} \text{ m}$$

[†] R.P. Feynman, R.B. Leighton and M. Sands, The Feynman Lectures on Physics, Vol III, Addison Wesley Publishing Co., 1965.

Therefore,

$$p \approx \Delta p \approx \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{5 \times 10^{-11}}$$

$$= 2.11 \times 10^{-24} \text{ kg m/s}$$

An electron having momentum of this order is nonrelativistic in behaviour. Therefore,

$$K = \frac{p^2}{2m}$$

$$= \frac{(2.11 \times 10^{-24})^2}{2 \times 9.1 \times 10^{-31}}$$

$$= 2.446 \times 10^{-18} \text{ J}$$

$$= 15.3 \text{ eV}$$

This value is reasonable.

Zero-Point Energy of a Harmonic Oscillator

We are familiar with the classical expression for the energy of a harmonic oscillator:

$$E = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

where ω is the angular frequency of oscillation. Classically, the minimum value of E is zero, which occurs when the particle is at rest ($p = 0$) at the mean position ($x = 0$). In quantum mechanics, the uncertainty principle does not allow this situation because then both position and momentum would be precisely known.

Let us assume that the particle is confined to a region of size a. Then

$$x \approx \Delta x \approx a$$

Using the exact statement of the uncertainty relation,

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

we get

$$p \approx \Delta p \approx \frac{\hbar}{2a}$$

The energy is then given by

$$E = \frac{\hbar^2}{8ma^2} + \frac{1}{2} m\omega^2 a^2 \tag{5.36}$$

For E to be minimum

$$\frac{dE}{da} = 0$$

which gives

$$a = [\hbar/2m\omega]^{1/2}$$

Substituting in (5.36), the minimum value of E is

$$E_{\min} = \frac{\hbar\omega}{2} \tag{5.37}$$

We shall see later, in a detailed study of the harmonic oscillator in chapter 9, that this is indeed the ground state energy of the harmonic oscillator. We used the exact statement of the uncertainty principle to get the right result.

This minimum energy is called the **zero-point energy**. It is clear that according to the uncertainty principle, no physical system can be completely at rest, even at absolute zero temperature. One important consequence of zero-point energy is that helium does not solidify even at very low temperatures, whereas normally a substance solidifies to form a crystal at low temperatures. Helium has a relatively shallow potential energy minimum. Moreover, being a light element, its kinetic energy is large. Therefore, it has large zero-point energy so that it remains in liquid form even at very low temperatures.

Broadening of Spectral Lines

Let us now consider an important example of the energy-time uncertainty relation (5.30). As mentioned earlier, this relation implies that a state of finite duration cannot have a precisely defined energy. Consider an atom in an excited state. We know that it de-exites in a very short span of time by emitting a photon. The statistical average time that elapses before the state de-exites is called the *lifetime* of that state. Let τ be the lifetime of the given excited state. From the uncertainty principle, the energy of this state is not sharply defined but is uncertain at least by an amount

$$\Delta E = \frac{\hbar}{\tau}$$

This is known as the *natural energy width* of the state. Clearly, shorter the lifetime of an excited state, larger is the natural energy width of that state. The ground state energy is sharply defined, that is it has zero energy width, because its lifetime is infinite.

Suppose the atom de-exites to the ground state. Due to the energy width of the excited state, the frequency of the emitted radiation will be spread by an amount

$$\Delta\nu = \frac{\Delta E}{h} = \frac{\hbar/\tau}{h} = \frac{1}{2\pi\tau}$$

Consequently, the spectral line is *broadened* (Figure 5.6). If the transition occurs between two excited states, then the broadening will be more pronounced because both the states have nonzero energy widths. The quantity $\Delta\nu$ is called the *natural linewidth* of the spectral line. We emphasize that this broading is a quantum mechanical phenomenon and cannot be explained classically. It is a consequence of the uncertainty principle.

The above discussion is not confined to atoms, but is equally applicable to other systems such as nuclei, molecules etc.

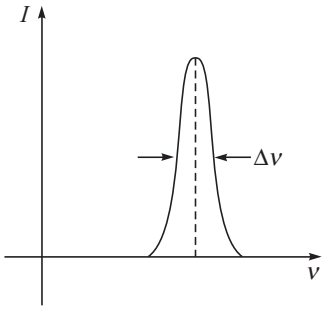


Figure 5.6 Broadening of a spectral line.

To get an idea of the numerical values, the lifetime of an atomic state is of order 10^{-8} s. Thus,

$$\Delta E = \frac{\hbar}{\tau} = \frac{1.054 \times 10^{-34}}{10^{-8}}$$
$$= 1.054 \times 10^{-26} \text{ J}$$

The width of the spectral line when the atom de-exites to the ground state is

$$\Delta \nu = \frac{\Delta E}{h}$$
$$= \frac{1.054 \times 10^{-26}}{6.3 \times 10^{-34}}$$
$$= 1.67 \times 10^{7} \text{ Hz}$$

This is the limit to the accuracy with which the frequency of the radiation emitted by an atom can be determined.

Mass of π-Meson

In 1935 Yukawa proposed that the nuclear force arises through the emission of a particle by one of the nucleons and its absorption by the other. This particle is now called π-meson or pion. If the mass of the pion is m, then its emission introduces an energy imbalance

$$\Delta E \approx mc^2$$

According to the uncertainty principle, this can take place only for a time

$$\Delta t \approx \frac{\hbar}{\Delta E} \approx \frac{\hbar}{mc^2}$$

The range covered by the pion before being absorbed is, therefore, of order

$$r_0 \approx c\,\Delta t \approx \frac{\hbar}{mc}$$

This yields

$$m \approx \frac{\hbar}{r_0 c}$$

or

$$\frac{m}{m_0} = \frac{1}{2\pi r_0}\left(\frac{h}{m_0 c}\right)$$

where m_0 is the mass of the electron. This gives

$$\frac{m}{m_0} \approx \frac{\lambda_0}{2\pi r_0}$$

where $\lambda_0 = h/m_0 c$ is the Compton wavelength of the electron (see section 2.3). Its value is 0.0242 Å. Substituting the values,

$$m \approx 275\, m_0$$

This estimated value is remarkably close to the actual value.

PROBLEM 5.2 Calculate the uncertainty in the momentum of a proton confined in a nucleus of radius 10^{-14} m. From this result, estimate the kinetic energy of the proton.

Solution: If the proton is confined within a nucleus of radius r_0, then the uncertainty in its momentum is

$$\Delta p \approx \frac{\hbar}{r_0} = \frac{1.054 \times 10^{-34}}{10^{-14}} = \boxed{1.054 \times 10^{-20}\ \text{kg m/s}}$$

Taking the momentum p to be of order Δp, the kinetic energy of the proton is given by

$$E = \frac{p^2}{2m} \approx \frac{\hbar^2}{2mr_0^2}$$

where m is the mass of the proton. Substituting the values,

$$\begin{aligned} E &\approx \frac{(1.054 \times 10^{-34})^2}{2 \times 1.67 \times 10^{-27} \times (10^{-14})^2} \\ &= 0.3326 \times 10^{-13}\ \text{J} \\ &= \frac{0.3326 \times 10^{-13}}{1.6 \times 10^{-13}}\ \text{MeV} \\ &= \boxed{0.21\ \text{MeV}} \end{aligned}$$

PROBLEM 5.3 An electron of energy 100 eV is passed through a slit of width 10^{-6} m. Estimate the uncertainty introduced in the angle of emergence.

Solution: The momentum of the electron is

$$p = \sqrt{2mE}$$

$$= \sqrt{2 \times 9.1 \times 10^{-31} \times 100 \times 1.6 \times 10^{-19}}$$
$$= 5.4 \times 10^{-24} \text{ kg m/s}$$

Uncertainty in momentum

$$\Delta p \approx \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{1 \times 10^{-6}}$$
$$= 1.054 \times 10^{-28} \text{ kg m/s}$$

Uncertainty in the angle of emergence

$$\Delta\theta \approx \frac{\Delta p}{p}$$
$$= \frac{1.054 \times 10^{-28}}{5.4 \times 10^{-24}} = 0.2 \times 10^{-4} \text{ radians}$$
$$\approx \boxed{4 \text{ seconds of arc}}$$

PROBLEM 5.4 Repeat Problem 5.3 for a lead ball of mass 0.2 g thrown with a speed of 10 m/s through a slit of radius 1.0 cm.

Solution: $p = 0.2 \times 10^{-3} \times 10 = 2 \times 10^{-3}$ kg m/s

$$\Delta p \approx \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{1.0 \times 10^{-2}}$$
$$= 1.054 \times 10^{-32} \text{ kg m/s}$$
$$\Delta\theta \approx \frac{\Delta p}{p} = \frac{1.054 \times 10^{-32}}{2 \times 10^{-3}}$$
$$= 5.3 \times 10^{-30} \text{ radians}$$
$$= \boxed{1.1 \times 10^{-24} \text{ seconds of arc}}$$

PROBLEM 5.5 The speed of a bullet of mass 50 g is measured to be 300 m/s with an accuracy of 0.01%. With what accuracy can we locate the position of the bullet?

Solution: $\Delta p = \Delta (mv) = m \, \Delta v$

$$= \frac{50}{1000} \times \frac{300 \times 0.01}{100}$$
$$= 1.5 \times 10^{-3} \text{ kg m/s}$$
$$\Delta x \approx \frac{\hbar}{\Delta p} = \frac{1.054 \times 10^{-34}}{1.5 \times 10^{-3}} = \boxed{7 \times 10^{-32} \text{ m}}$$

PROBLEM 5.6 The lifetime of a nucleus in an excited state is 10^{-12} s. Calculate the probable uncertainty in the energy and frequency of a γ-ray photon emitted by it.

Solution: The energy-time uncertainty relation is

$$\Delta E\ \Delta t \approx \hbar$$

Therefore, the uncertainty in energy is

$$\Delta E \approx \frac{\hbar}{\Delta t} = \frac{1.054 \times 10^{-34}}{10^{-12}} = \boxed{1.054 \times 10^{-22}\ \text{J}}$$

The uncertainty in frequency is

$$\Delta \nu = \frac{\Delta E}{h} = \frac{1.054 \times 10^{-22}}{6.625 \times 10^{-34}} = \boxed{1.59 \times 10^{11}\ \text{Hz}}$$

PROBLEM 5.7 Using the uncertainty principle, show that an alpha particle can exist inside a nucleus.

Solution: The radius of a typical nucleus is of the order of 10^{-14} m. If a particle is to exist within the nucleus, then the uncertainty in its position must be of this order:

$$\Delta x \approx 10^{-14}\ \text{m}$$

Therefore, the uncertainty in the momentum of the particle must be

$$\Delta p \approx \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{10^{-14}}$$
$$= 1.054 \times 10^{-20}\ \text{kg m/s}$$

The momentum of the particle is at least of this order.

The rest mass of an α-particle is approximately four times the mass of a proton:

$$m = 4 \times 1.67 \times 10^{-27}\ \text{kg}$$

The speed of the α-particle would be

$$v = \frac{1.054 \times 10^{-20}}{4 \times 1.67 \times 10^{-27}} = 1.58 \times 10^{6}\ \text{m/s}$$

With this speed the motion can be considered nonrelativistic. Therefore, the kinetic energy of the particle is at least

$$K = \frac{p^2}{2m} = \frac{(1.054 \times 10^{-20})^2}{2 \times 4 \times 1.67 \times 10^{-27}}$$
$$= 8.3 \times 10^{-15}\ \text{J}$$
$$= \boxed{52\ \text{keV}}$$

Energy carried by α-particles emitted by nuclei is much more than this value. Thus, α-particles can exist inside a nucleus.

PROBLEM 5.8 A nucleon (neutron or proton) is confined to a nucleus of radius 5×10^{-15} m. Calculate the minimum possible values of the momentum and the kinetic energy of the nucleon.

Solution: The maximum uncertainty in the position of the nucleon is

$$(\Delta x)_{\max} = 2 \times 5 \times 10^{-15} = 10^{-14} \text{ m}$$

According to the uncertainty principle, the minimum uncertainty in the momentum of the particle is

$$(\Delta p)_{\min} \approx \frac{\hbar}{(\Delta x)_{\max}} = \frac{1.05 \times 10^{-34}}{10^{-14}}$$
$$= 1.05 \times 10^{-20} \text{ kg m/s}$$

The momentum cannot be less than this value. Thus,

$$p_{\min} = (\Delta p)_{\min} = \boxed{1.05 \times 10^{-20} \text{ kg m/s}}$$

The minimum kinetic energy is, therefore,

$$K_{\min} = \frac{p_{\min}^2}{2m} = \frac{(1.05 \times 10^{-20})^2}{2 \times 1.67 \times 10^{-27} \times 1.6 \times 10^{-13}} \text{ MeV}$$
$$= \boxed{0.2 \text{ MeV}}$$

PROBLEM 5.9 If the angular momentum of the electron in a hydrogen atom is known to be $2\hbar$ within 5% accuracy, show that its angular position in a perpendicular plane cannot be specified at all.

Solution: According to the uncertainty principle,

$$\Delta L \Delta\theta \approx \hbar$$

Here
$$\Delta L = \frac{5}{100}(2\hbar) = \frac{\hbar}{10}$$

Therefore,
$$\Delta\theta = \frac{\hbar}{\Delta L} = 10 \text{ radians}$$

Since the angle in a plane cannot be greater than 2π, it is clear that the angular position of the electron cannot be specified.

PROBLEM 5.10 The average lifetime of an excited atomic state is 10^{-8} s. If the wavelength of the spectral line associated with the transition from this state to the ground state is 6000 Å, estimate the width of this line.

Solution: We have

$$E = h\nu = \frac{hc}{\lambda}$$

or $$\Delta E = \frac{hc}{\lambda^2}\ \Delta\lambda$$

According to the uncertainty principle,

$$\Delta E \Delta t \approx \hbar$$

or $$\frac{hc}{\lambda^2}\Delta\lambda\Delta t \approx \hbar$$

or $$\Delta\lambda = \frac{\lambda^2}{2\pi c\,\Delta t}$$

$$= \frac{(6\times10^{-7})^2}{2\times3.14\times3\times10^{8}\times10^{-8}}$$

$$= \boxed{1.9\times10^{-14}\ \text{m}}$$

PROBLEM 5.11 Using the uncertainty principle, estimate the ground state energy of the helium atom.

Solution: Helium atom has two electrons. Let the regions of localization of the two electrons have dimensions r_1 and r_2. Then the spread in momenta, and therefore, the minimum momenta, of the two electrons would be

$$p_1 \approx \frac{\hbar}{r_1},\ p_2 \approx \frac{\hbar}{r_2}$$

The kinetic energy of the system is

$$\approx \frac{\hbar^2}{2m}\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)$$

where m is the mass of the electron. The potential energy of the interaction of the electrons with the nucleus of charge $2e$ is $\approx -2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$. Finally, since the separation between the electrons is of order $(r_1 + r_2)$, the interaction energy between the electrons is $\approx e^2/(r_1 + r_2)$. The total energy of the system is, therefore,

$$E \approx \frac{\hbar^2}{2m}\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right) - 2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{r_1+r_2}$$

In the ground state E is minimum. Therefore,

$$\frac{dE}{dr_1} = -\frac{\hbar^2}{mr_1^3} + \frac{2e^2}{r_1^2} - \frac{e^2}{(r_1+r_2)^2} = 0$$

and $$\frac{dE}{dr_2} = -\frac{\hbar^2}{mr_2^3} + \frac{2e^2}{r_2^2} - \frac{e^2}{(r_1+r_2)^2} = 0$$

Solving these equations, we get

$$r_1 = r_2 = \frac{4}{7}\frac{\hbar^2}{me^2}$$

Substituting in the expression for E and simplifying, the total energy in the ground state is

$$\begin{aligned} E &\approx -\frac{49}{16}\frac{me^4}{\hbar^2} \\ &= -\frac{49}{16}\left(\frac{9.1\times10^{-31}\times(1.6\times10^{-19})^4}{(1.05\times10^{-34})^2\times1.6\times10^{-19}}\right)\text{ eV} \\ &= \boxed{-10.35\text{ eV}} \end{aligned}$$

SUMMARY

1. If a wave is to be associated with a particle, then its amplitude should be sizeable only in the neighborhood of the particle. Therefore, a particle can be represented by a wave packet. A wave packet is formed by superposing plane waves of different wave numbers, and hence momenta, in such a way that they interfere with each other destructively outside of a given region of space. A wave packet in one dimension is written as

$$\Psi(x,\ t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\phi(p)\,e^{(i/\hbar)(px-Et)}\,dp$$

where $\phi(p)$ is negligible outside a small momentum range. If we define

$$\Phi(p,\ t) = \phi(p)\,e^{-iEt/\hbar}$$

then

$$\Phi(p,\ t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\Psi(x,\ t)\,e^{-ipx/\hbar}\,dx$$

$\Psi(x,\ t)$ and $\Phi(p,\ t)$, which are Fourier transforms of each other, are known as the *wave functions in coordinate space and momentum space*, respectively. They satisfy

$$\int_{-\infty}^{\infty}|\Psi(x,\ t)|^2\,dx = \int_{-\infty}^{\infty}|\Phi(p,\ t)|^2\,dp = 1$$

2. The group velocity of a wave packet is equal to the velocity of the particle, both in the nonrelativistic and relativistic cases.

3. It follows from the properties of a wave packet that

$$\Delta x\Delta p \geq \hbar$$

This is Heisenberg's uncertainty relation for position and momentum. Heisenberg recognized the uncertainty principle as a general principle that underlies the structure of quantum mechanics. The statement is:

It is impossible to simultaneously specify the precise values of both members of certain pairs of dynamical variables of a system. These variables, called complementary variables, are canonically conjugate to each other, e.g., position-momentum, energy-time etc. The product of the uncertainties in the values of the two variables is at least of the order of $\hbar$.

4. Single and double-slit diffraction experiments with particles and Heisenberg's gamma-ray microscope, which is a thought experiment, provide illustrations of the uncertainty principle.
5. Some important application/consequences of the uncertainty principle are:
   (a) Estimation of the ground state energy and radius of the hydrogen atom;
   (b) Nonexistence of electrons inside the nucleus;
   (c) Existence of zero-point energy of a harmonic oscillator;
   (d) Broadening of spectral lines;
   (e) Estimation of the mass of π-meson.

QUESTIONS

1. What is a wave packet? Discuss the representation of a material particle by a wave packet.
2. What is meant by the phase velocity and the group velocity of a wave packet? Show that the phase velocity has no physical significance and the group velocity is identical with the velocity of the particle both in the nonrelativistic and relativistic cases.
3. (a) State Heisenberg's uncertainty relation for position and momentum.
   (b) Illustrate the uncertainty principle by Heisenberg's gamma-ray microscope.
4. Describe how the single-slit diffraction experiment using an electron beam illustrates the uncertainty principle.
5. Describe the double-slit experiment using an electron beam. Show that the results of this experiment can be explained only if the uncertainty principle is assumed to be valid.
6. State the energy-time uncertainty relation. Explain how the broadening of spectral lines can be explained using this relation.
7. Explain the uncertainty principle. Give its general statement.
8. Use the uncertainty principle to show that electrons cannot exist inside a nucleus.

9. Estimate the ground state energy and the radius of the hydrogen atom using uncertainty principle.

10. Show that the zero-point energy of a harmonic oscillator is a consequence of the uncertainty principle.

11. Use the energy-time uncertainty relation to estimate the mass of the π-meson (pion).

EXERCISES

1. An electron is confined to a box of length 10^{-8} m. Estimate the uncertainty in the measurement of its speed. Mass of electron = 9.0×10^{-31} kg. [***Ans.*** 1.17×10^{-4} m/s]

2. An electron in the $n = 2$ state of a hydrogen atom remains there on an average for about 10^{-8} s before making a transition to the ground state.

(a) Estimate the uncertainty in the energy of the $n = 2$ state.
(b) What fraction of the transition energy is this?
(c) What is the width of the spectral line emitted in the transition?

[***Ans.*** (a) 4.14×10^{-7} eV, (b) 4.06×10^{-8}, (c) 4.95×10^{-5} Å]

3. A bullet of mass 0.03 kg is moving with a speed of 500 m/s. The speed is measured with an accuracy of 0.02%. Using the uncertainty principle, estimate the uncertainty in the measurement of its position.

[***Ans.*** 2.2×10^{-31} m]

4. Compare the uncertainties in the velocities of an electron and a proton when restricted to a 10 F box. Their masses are 9.1×10^{-31} kg and 1.67×10^{-27} kg, respectively.

$$\left[\textbf{\textit{Ans.}} \quad \frac{(\Delta v)_{\text{electron}}}{(\Delta v)_{\text{proton}}} = \frac{m_{\text{proton}}}{m_{\text{electron}}} = 1835 \right]$$

5. From considerations of the uncertainty principle, find the ground state energy of a particle of mass m trapped in a one-dimensional box of length L. [***Ans.*** $\hbar^2/2mL^2$]

Chapter

6 The Schrödinger Equation

Chapter Contents

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6.8 The Time-Independent Schrödinger Equation. Stationary States
6.9 The Free Particle

6.1 THE NECESSITY FOR A WAVE EQUATION AND CONDITIONS IMPOSED ON IT

In chapter 4 we introduced the concept of the wave function $\Psi(\mathbf{r}, t)$, which is assumed to describe the dynamical state of a particle (or a physical system) completely. In chapter 5 we saw that a particle can be represented by a wave packet which is formed by superposing plane waves of different wave numbers. However, it is clear that in order to make further progress, we must have a method of determining wave functions in a systematic manner. For this, we need a wave equation, solving which we may obtain the wave function at any point $(\mathbf{r}, t)$ in space and time, given suitable initial and boundary conditions.

It is obvious that such an equation cannot be derived. Like all fundamental equations of physics, it must be *guessed* or arrived at in a *heuristic* manner. It must then be adopted as a *postulate*, the justification for which lies in the closeness of its predictions to the experimental results.

The equation must satisfy the following restrictions:

1. It must be *linear* and *homogeneous* so that the *superposition principle* holds. That is, if Ψ_1 and Ψ_2 are solutions of the equation, any linear combination $a_1\Psi_1 + a_2\Psi_2$ must also be a solution.
2. It must be a differential equation of the first order with respect to time, so that the evolution of the system is completely determined if the wave function is known at a given initial time.
3. It must be consistent with the Planck-Einstein relation $E = \hbar\omega$, the de Broglie relation $\mathbf{p} = \hbar\mathbf{k}$, and the correspondence principle.

The equation was discovered by Erwin Schrödinger in 1926 and is called the *Schrödinger equation*. Without going into the details of how Schrödinger discovered it, we shall arrive at this equation starting from a plane wave/wave packet.

6.2 THE TIME-DEPENDENT SCHRÖDINGER EQUATION

To begin with, we consider the one-dimensional motion of a free particle of mass m, moving in the positive x direction with momentum p and energy E. Such a particle can be described by the monochromatic plane wave

$$\Psi(x, t) = A\, e^{i(px - Et)/\hbar} \tag{6.1}$$

where A is a constant. Differentiating with respect to t, we have

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar}\Psi$$

or

$$i\hbar\frac{\partial \Psi}{\partial t} = E\Psi \tag{6.2}$$

Differentiating twice with respect to x, we have

$$-i\hbar\frac{\partial \Psi}{\partial x} = p\Psi \tag{6.3}$$

and

$$-\hbar^2\frac{\partial^2 \Psi}{\partial x^2} = p^2\Psi$$

or

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m}\Psi \tag{6.4}$$

Now, for a nonrelativistic free particle

$$E = \frac{p^2}{2m} \tag{6.5}$$

Therefore, (6.2), (6.4) and (6.5) give

$$\boxed{i\hbar\frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x, t)}{\partial x^2}} \tag{6.6}$$

This is the *one-dimensional time-dependent Schrödinger equation for a free particle*.

Since (6.6) is linear and homogeneous, it will also be satisfied by the wave packet

$$\Psi(x,\ t) = \frac{1}{\sqrt{2\pi\hbar}} \int \phi(p)\, e^{i(px-Et)/\hbar}\, dp \tag{6.7}$$

which is a linear superposition of plane waves and is associated with a 'localised' free particle. We have

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \frac{1}{\sqrt{2\pi\hbar}} \int E\phi(p)\, e^{i(px-Et)/\hbar}\, dp$$

and

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{\sqrt{2\pi\hbar}} \int \frac{p^2}{2m} \phi(p)\ \ e^{i(px-Et)/\hbar}\, dp$$

Using (6.5), the right hand sides of the above two equations are equal, and hence we obtain (6.6).

It is clear that the Schrödinger equation for a free particle satisfies the three restrictions that we mentioned in section 6.1. To see how it satisfies the correspondence principle, we note that this equation is, in a sense, the quantum mechanical 'translation' of the classical equation (6.5), where the energy E, and the momentum p are represented by **differential operators**[†]

$$\boxed{\hat{E} = i\hbar \frac{\partial}{\partial t}} \tag{6.8}$$

and

$$\boxed{\hat{p} = -i\hbar \frac{\partial}{\partial x}} \tag{6.9}$$

respectively, acting on the wave function:

$$\hat{E}\, \Psi(x,\ t) = \frac{\hat{p}^2}{2m} \Psi(x,\ t) \tag{6.10}$$

As we shall see later, it is a *postulate* of quantum mechanics that even when the particle is not free, E and p are still represented by the operators in (6.8) and (6.9), respectively.

The above treatment can be easily extended to three dimensions. Instead of (6.1), the expression for the plane wave is

$$\Psi(\mathbf{r},\ t) = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} \tag{6.11}$$

The **operator representation** of $\mathbf{p}$ would be

$$\boxed{\hat{\mathbf{p}} = -i\hbar\nabla} \tag{6.12}$$

[†] It is customary to represent a variable and its operator by the same symbol. Wherever there is confusion, a hat is put on the symbol to represent the operator, e.g., $\hat{E}$, $\hat{p}$.

which is equivalent to

$$\boxed{\begin{aligned}\hat{p}_x &= -i\hbar\frac{\partial}{\partial x}\\ \hat{p}_y &= -i\hbar\frac{\partial}{\partial y}\\ \hat{p}_z &= -i\hbar\frac{\partial}{\partial z}\end{aligned}} \tag{6.13}$$

Therefore, the Schrödinger equation becomes

$$\boxed{i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t)} \tag{6.14}$$

where $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Particle in a Force-field

Let us now generalize the free-particle Schrödinger equation (6.14) to the case of a particle acted upon by a force which is derivable from a potential $V(\mathbf{r}, t)$. According to classical mechanics, the total energy of the particle would be given by

$$E = \frac{p^2}{2m} + V(\mathbf{r}, t) \tag{6.15}$$

Since V does not depend on E or $\mathbf{p}$, the above discussion for the free particle suggests that the wave function should satisfy

$$\hat{E}\Psi = \left(\frac{\hat{p}^2}{2m} + V\right)\Psi$$

so that, the Schrödinger equation generalizes to

$$\boxed{\begin{aligned}&i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left(-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r},t)\right)\Psi(\mathbf{r},t)\\ &\textbf{(Time-dependent Schrödinger equation)}\end{aligned}} \tag{6.16}$$

The operator on the right-hand side is called the *Hamiltonian operator* and is denoted by the symbol H:

$$\boxed{\begin{aligned}&H = -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r},t)\\ &\textbf{(Hamiltonian operator)}\end{aligned}} \tag{6.17}$$

The name follows from the fact that in classical mechanics the sum of the kinetic and the potential energies of a particle is called its *Hamiltonian*.

The Schrödinger Equation (6.16), is the *basic equation* of nonrelativistic quantum mechanics. It must be emphasized that we have *not derived* it. Like

any basic law, this equation cannot be proved to be true. Its justification comes from successful comparison of the predictions based on it with experimental results in a large number of situations.

6.3 STATISTICAL INTERPRETATION OF THE WAVE FUNCTION AND CONSERVATION OF PROBABILITY

As we have already discussed in section 4.5, the wave function associated with a particle has a statistical interpretation, first given by Max Born. The interpretation is as follows: If a particle is described by a wave function $\Psi(\mathbf{r}, t)$, then the probability of finding the particle, at time t, within the volume element $d\mathbf{r} = dxdydz$ about the point $\mathbf{r} \equiv (x, y, z)$ is

$$P(\mathbf{r}, t)\, d\mathbf{r} = |\Psi(\mathbf{r}, t)|^2\, d\mathbf{r} = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\, d\mathbf{r} \tag{6.18}$$

The quantity

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t) \tag{6.19}$$

is obviously called the **position probability density**. Since the probability of finding the particle somewhere at time t is unity, the wave function is chosen to satisfy the **normalization condition**

$$\boxed{\int |\Psi(\mathbf{r}, t)|^2\, d\mathbf{r} = 1} \tag{6.20}$$

where the integral extends over all space. The wave functions for which the above integral exists are said to be *square integrable*. It may be noted here that some wave functions, for example the plane wave (6.11), are not square integrable. A plane wave represents a free particle which has a well-defined momentum and is, therefore, completely 'delocalized' according to the uncertainty principle. However, we have seen that this difficulty can be overcome if the requirement that a particle should have a well-defined momentum is given up. We then obtain a 'localized' wave packet, which can be normalized to unity. In this book we shall be mainly concerned with square integrable wave functions. However, plane waves provide useful representation of particles in certain situations. We shall briefly discuss methods of normalizing such functions in section 6.9.

Let us now see what happens as time changes. It is clear that the probability of finding the particle somewhere must remain *conserved*. That is, the normalization integral in (6.20) must be independent of time:

$$\frac{\partial}{\partial t} \int P(\mathbf{r}, t) d\mathbf{r} = \frac{\partial}{\partial t} \int \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t) d\mathbf{r} = 0 \tag{6.21}$$

where the integral extends over all space.

In order to prove this, we use the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \tag{6.22}$$

and its complex conjugate

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^* \tag{6.23}$$

where $V(\mathbf{r}, t)$ is assumed to be real.

Multiplying (6.22) by Ψ^* and (6.23) by Ψ on the left and then subtracting, we get

$$i\hbar\left[\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\Psi^*}{\partial t}\right] = -\frac{\hbar^2}{2m}[\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*] \tag{6.24}$$

Now, consider the time derivative of the integral of $\Psi^*\Psi$ over a finite volume V. We have,

$$\frac{\partial}{\partial t}\int_V \Psi^*\Psi d\mathbf{r} = \int_V\left[\left(\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\Psi^*}{\partial t}\right)\right]d\mathbf{r}$$

$$= \frac{i\hbar}{2m}\int_V [(\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*)]d\mathbf{r} \qquad \text{(using 6.24)}$$

$$= \frac{i\hbar}{2m}\int_V \boldsymbol{\nabla}\cdot(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*)d\mathbf{r} \tag{6.25}$$

Let us define a vector

$$\boxed{\mathbf{j}(\mathbf{r}, t) = \frac{\hbar}{2im}(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*)} \tag{6.26}$$

Substituting in (6.25),

$$\frac{\partial}{\partial t}\int_V P(\mathbf{r}, t)\, d\mathbf{r} = -\int_V \boldsymbol{\nabla}\cdot\mathbf{j}\, d\mathbf{r} \tag{6.27}$$

Using Green's theorem (also called Gauss' divergence theorem) we can convert the volume integral on the right into an integral over the surface S bounding the volume V:

$$\frac{\partial}{\partial t}\int_V P(\mathbf{r}, t)d\mathbf{r} = -\int_S \mathbf{j}\cdot d\mathbf{S} \tag{6.28}$$

where the vector $d\mathbf{S}$ has magnitude equal to an element dS of the surface S and is directed along the outward normal to dS.

When V is the entire space, as is the case in the normalization integral, the surface S in (6.28) recedes to infinity. Since a square integrable wave function vanishes at large distances, the surface integral becomes zero and hence (6.21) is proved.

Probability Conservation and the Hermiticity of the Hamiltonian

We shall now show that the conservation of probability implies that the Hamiltonian operator H appearing in the Schrödinger equation is Hermitian.

In terms of H, the Schrödinger equation can be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \tag{6.29}$$

The complex conjugate of this equation is

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = (H\Psi)^* \tag{6.30}$$

Using these equations, we can write

$$\frac{\partial}{\partial t}\int \Psi^*\Psi d\mathbf{r} = \int\left(\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}\right) d\mathbf{r}$$

$$= (i\hbar)^{-1}\int [\Psi^*(H\Psi) - \Psi(H\Psi)^*] d\mathbf{r}$$

Since the left-hand side is zero, we obtain

$$\boxed{\int \Psi^*(H\Psi) d\mathbf{r} = \int (H\Psi)^* \Psi \, d\mathbf{r}} \tag{6.31}$$

Operators which satisfy this condition are called **Hermitian operators**. Thus, H is an Hermitian operator. The significance of Hermitian operators in quantum mechanics will become clear in chapter 10.

Probability Current Density

Let us now look at (6.28) again. It says that the rate of change of the probability of finding the particle in a volume V is equal to the probability flux passing through the surface S bounding V. It is reasonable, therefore, to interpret the vector $\mathbf{j}(\mathbf{r}, t)$ as *probability current density* (or simply *probability current* as some books do). This is further clear from (6.27). Since this equation is true for any arbitrary volume, we have

$$\boxed{\frac{\partial}{\partial t} P(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0} \tag{6.32}$$

This equation has the familiar form associated with the conservation of matter in a fluid of density P and current density $\mathbf{j}$ in a medium in which there are no sources or sinks. This is called the **equation of continuity**.

If $\nabla \cdot \mathbf{j}$ is zero in a state, then for that state the probability density is constant in time. Such states are called **stationary states**.

The probability current density (6.26) may also be written as

$$\boxed{\mathbf{j}(\mathbf{r}, t) = \mathrm{Re}\left[\Psi^* \frac{\hbar}{im} \nabla \Psi\right]} \tag{6.33}$$

where 'Re' indicates 'real part of'.

It may be noted that the operator $(\hbar/im)\nabla$ represents $\mathbf{p}/m$, that is, the velocity $\mathbf{v}$ of the particle. Thus, $\mathbf{j}$ corresponds to the product of the probability density P and the velocity $\mathbf{v}$:

$$\mathbf{j} = P\mathbf{v}$$

Thus, it is appropriate to interpret $\mathbf{j}$ as a probability current density.

It may further be noted that **j** vanishes if Ψ is real. Therefore, for describing situations in which the probability current is nonzero, it is necessary to use complex wave functions.

6.4 EXPECTATION VALUES OF DYNAMICAL VARIABLES

We have seen that in quantum mechanics a particle is represented by a wave function which can be obtained by solving the Schrödinger equation and contains all the available information about the particle. We shall now see how information concerning the dynamical variables of the particle can be extracted from the wave function Ψ. Since Ψ has a probabilistic interpretation, it turns out that exact information about the variables cannot be obtained. Instead, we obtain only the *expectation value* of a quantity, which is the average value of the measurements of the quantity performed on a very large number of independent identical systems represented by the wave function Ψ. Or, equivalently, it is the average of a large number of measurements on the same system.

First, let us consider the measurement of the position of the particle. Since $P(\mathbf{r}, t) = \Psi^*(\mathbf{r}, t)\,\Psi(\mathbf{r}, t)$ is interpreted as the position probability density at the point $\mathbf{r}$ at the time t, the *expectation value* of the position vector $\mathbf{r}$ is given by

$$\langle \mathbf{r} \rangle = \int \mathbf{r}\, P(\mathbf{r}, t)\, d\mathbf{r}$$

$$= \int \Psi^*(\mathbf{r}, t)\, \mathbf{r}\, \Psi(\mathbf{r}, t)\, d\mathbf{r} \tag{6.34}$$

where $\Psi(\mathbf{r}, t)$ is normalized. This equation is equivalent to the three equations

$$\langle x \rangle = \int \Psi^*\, x\, \Psi\, d\mathbf{r} \tag{6.35a}$$

$$\langle y \rangle = \int \Psi^*\, y\, \Psi\, d\mathbf{r} \tag{6.35b}$$

$$\langle z \rangle = \int \Psi^*\, z\, \Psi\, d\mathbf{r} \tag{6.35c}$$

The expectation value is a function only of the time because the space coordinates have been integrated out. Further, the expectation value of a physical quantity is always real. Note the order of the factors in the integrand—the vector $\mathbf{r}$ (or each of x, y, z) has been sandwitched between Ψ^* on the left and Ψ on the right. This is immaterial at this stage but is chosen for reason which will be clear shortly.

The *expectation value* of any quantity which is a function of $\mathbf{r}$ and t would be

$$\boxed{\langle f(\mathbf{r}, t) \rangle = \int \Psi^*(\mathbf{r}, t)\, f(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\, d\mathbf{r}} \tag{6.36}$$

As an example, the expectation value of the potential energy is

$$\langle V(\mathbf{r}, t)\rangle = \int \Psi^*(\mathbf{r}, t)\, V(\mathbf{r}, t)\, \Psi(\mathbf{r}, t) d\mathbf{r} \tag{6.37}$$

Let us now see how to obtain the expectation values for quantities which are functions of momentum or of both position and momentum. The most important example of the latter category is the energy. We assume that for this purpose it is possible to use the operator representations:

$$\hat{\mathbf{p}} = -i\hbar\, \boldsymbol{\nabla}$$

$$p^2 = -\hbar^2\, \nabla^2$$

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

The question that arises is: How these differential operators are to be combined with the position probability density $\Psi^*\Psi$ to obtain the desired expressions? This question is answered by using the classical expression for the energy

$$E = \frac{p^2}{2m} + V$$

and requiring, in accordance with the correspondence principle, that the expectation values satisfy

$$\langle E\rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V\rangle$$

Replacing E and p^2 by the corresponding operators, we get

$$\left\langle i\hbar \frac{\partial}{\partial t} \right\rangle = \left\langle -\frac{\hbar^2}{2m} \nabla^2 \right\rangle + \langle V\rangle \tag{6.38}$$

This equation must be consistent with the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2 \nabla^2}{2m}\, \Psi + V\Psi$$

Multiplying by Ψ^* on the left and integrating, we get

$$\int \Psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \Psi d\mathbf{r} = \int \Psi^* \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \Psi d\mathbf{r} + \int \Psi^* V \Psi\, d\mathbf{r} \tag{6.39}$$

The last term on the right-hand side is simply $\langle V\rangle$. Therefore, (6.38) and (6.39) would be consistent provided the *expectation value is defined in the general case with the operator acting on* Ψ*, and multiplied by* Ψ^* *on the left.* We then have

$$\langle E\rangle = \int \Psi^*\, i\hbar\, \frac{\partial \Psi}{\partial t} d\mathbf{r} \tag{6.40}$$

$$\langle \mathbf{p}\rangle = \int \Psi^*\, (-i\hbar)\, \boldsymbol{\nabla} \Psi\, d\mathbf{r} \tag{6.41}$$

The last equation is equivalent to

$$\langle p_x \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x}\, d\mathbf{r} \tag{6.42a}$$

$$\langle p_y \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial y}\, d\mathbf{r} \tag{6.42b}$$

$$\langle p_z \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial z}\, d\mathbf{r} \tag{6.42c}$$

Generalizing the above results, we are led to the following *postulate*:

Suppose, the dynamical state of a particle is described by the normalized wave function $\Psi(\mathbf{r}, t)$. Let $A(\mathbf{r}, \mathbf{p}, t)$ be a dynamical variable representing a physical quantity associated with the particle. We obtain the operator $\hat{A}(\mathbf{r}, -i\hbar\nabla, t)$ by performing the substitution $\mathbf{p} \to -i\hbar\nabla$, and then calculate the expectation value of A from the expression

$$\boxed{\langle A \rangle = \int \Psi^*(\mathbf{r}, t)\, \hat{A}(\mathbf{r}, -i\hbar\nabla, t)\, \Psi(\mathbf{r}, t)\, d\mathbf{r}} \tag{6.43}$$

Since the expectation value of a physical quantity is always *real*, i.e., $\langle A \rangle^* = \langle A \rangle$, it follows that the operator $\hat{A}$ must satisfy

$$\boxed{\int \Psi^* \hat{A} \Psi\, d\mathbf{r} = \int (\hat{A}\Psi)^*\, \Psi\, d\mathbf{r}} \tag{6.44}$$

Thus, the operator associated with a dynamical quantity must be *Hermitian.*

6.5 MOTION OF WAVE PACKETS: EHRENFEST'S THEOREM

According to the correspondence principle, it is reasonable to expect that the average motion of a wave packet should agree with the motion of a classical particle. In 1927, P. Ehrenfest showed that this is actually the case. According to Ehrenfest's theorem, *the equations of motion of the expectation values of the position and momentum vectors for a wave packet are formally identical to Newton's equations of classical mechanics*. That is,

$$\boxed{\frac{d}{dt}\langle \mathbf{r} \rangle = \frac{\langle \mathbf{p} \rangle}{m}} \tag{6.45}$$

and

$$\boxed{\frac{d}{dt}\langle \mathbf{p} \rangle = -\langle \nabla V \rangle} \tag{6.46}$$

Proof of (6.45)

In order to prove (6.45), let us first consider the expectation value of the x-component of the position vector $\mathbf{r}$. Assuming that the wave function Ψ representing the wave packet is normalized to unity, we have

$$\langle x \rangle = \int \Psi^* x \Psi\, d\mathbf{r}$$

The time rate of change of $\langle x \rangle$ is

$$\frac{d}{dt}\langle x \rangle = \frac{d}{dt}\int \Psi^* x \Psi \, d\mathbf{r}$$

$$= \int \Psi^* x \frac{\partial \Psi}{\partial t} d\mathbf{r} + \int \frac{\partial \Psi^*}{\partial t} x \Psi d\mathbf{r}$$

The right-hand side can be transformed by using the Schrödinger equation (6.22) and its complex conjugate (6.23). We obtain

$$\frac{d}{dt}\langle x \rangle = \frac{1}{i\hbar}\left[\int \Psi^* x \left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi\right)d\mathbf{r} - \int\left(-\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^*\right)x\Psi \, d\mathbf{r}\right.$$

$$= \frac{i\hbar}{2m}\int [\Psi^* x \, (\nabla^2\Psi) - (\nabla^2\Psi^*)x \, \Psi] \, d\mathbf{r} \tag{6.47}$$

Let us consider the second part of the integral. Using Green's first identity[†], we obtain

$$\int (\nabla^2\Psi^*)x\Psi d\mathbf{r} = \int_S x\Psi(\boldsymbol{\nabla}\Psi^*)\cdot d\mathbf{S} - \int (\boldsymbol{\nabla}\Psi^*)\cdot\boldsymbol{\nabla}(x\Psi)d\mathbf{r}$$

Since the volume under consideration is the entire space, the surface S in the first integral on the right is at infinity. Hence, this integral is zero because the wave function vanishes at large distances. Therefore,

$$\int (\nabla^2\Psi^*)x\Psi d\mathbf{r} = -\int (\boldsymbol{\nabla}\Psi^*)\cdot\boldsymbol{\nabla}(x\Psi) \, d\mathbf{r}$$

Using Green's first identity again, we get

$$-\int (\boldsymbol{\nabla}\Psi^*)\cdot\boldsymbol{\nabla}(x\Psi)d\mathbf{r} = -\int_S \Psi^*\boldsymbol{\nabla}(x\Psi)\cdot d\mathbf{S} + \int \Psi^* \, \nabla^2(x\Psi) \, d\mathbf{r}$$

The surface integral again vanishes. Thus,

$$\int (\nabla^2\Psi^*)x\Psi d\mathbf{r} = \int \Psi^* \, \nabla^2(x\Psi) \, d\mathbf{r}$$

Substituting this back into (6.47), we obtain

$$\frac{d}{dt}\langle x \rangle = \frac{i\hbar}{2m}\int \Psi^*[x\nabla^2\Psi - \nabla^2(x\Psi)]d\mathbf{r}$$

It can be easily shown that

$$\nabla^2(x\Psi) = x\nabla^2\Psi + 2\frac{\partial\Psi}{\partial x}$$

[†] Green's first identity: If f and g are scalar functions of position, then

$$\int_V [f\,\nabla^2 g + (\boldsymbol{\nabla}f)\cdot(\boldsymbol{\nabla}g)]d\mathbf{r} = \int_S f(\boldsymbol{\nabla}g)\cdot d\mathbf{S}$$

where V is the volume bounded by the closed surface S. For our case, take $f = x\Psi$ and $g = \Psi^*$.

Therefore,

$$\frac{d}{dt}\langle x\rangle = -\frac{i\hbar}{m}\int \Psi^* \frac{\partial \Psi}{\partial x}\, d\mathbf{r}$$

$$= \frac{1}{m}\int \Psi^* \left(-i\hbar \frac{\partial}{\partial x}\right)\Psi\, d\mathbf{r}$$

$$= \frac{\langle p_x \rangle}{m}$$

Similarly, we can prove that

$$\frac{d}{dt}\langle y\rangle = \frac{\langle p_y \rangle}{m},\ \frac{d}{dt}\langle z\rangle = \frac{\langle p_z \rangle}{m}$$

These three equations are the three components of Equation (6.45), which was to be proved.

Proof of (6.46)

Let us calculate the time rate of change of the expectation value of the x-component of the momentum of the particle. We have

$$\frac{d}{dt}\langle p_x \rangle = -i\hbar \frac{d}{dt}\int \Psi^* \frac{\partial \Psi}{\partial t}\, d\mathbf{r}$$

$$= -i\hbar\left[\int \Psi^* \frac{\partial}{\partial x}\frac{\partial \Psi}{\partial t}\, d\mathbf{r} + \int \frac{\partial \Psi^*}{\partial t}\frac{\partial \Psi}{\partial x}\, d\mathbf{r}\right]$$

Using the Schrödinger equation (6.22) and its complex conjugate (6.23) to replace $\partial\Psi/\partial t$ and $\partial\Psi^*/\partial t$, respectively, we get

$$\frac{d}{dt}\langle p_x \rangle = -\int \Psi^* \frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi\right)d\mathbf{r} + \int\left(-\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^*\right)\frac{\partial \Psi}{\partial x}\, d\mathbf{r}$$

$$= \frac{\hbar^2}{2m}\int\left[\Psi^*\left(\nabla^2 \frac{\partial \Psi}{\partial x}\right) - (\nabla^2\Psi^*)\frac{\partial \Psi}{\partial x}\right]d\mathbf{r} - \int \Psi^*\left[\frac{\partial}{\partial x}(V\Psi) - V\frac{\partial \Psi}{\partial x}\right]d\mathbf{r}$$

Using Green's second identity[†] the first integral on the right is zero because Ψ and $\partial\Psi/\partial x$ vanish at large distances. The second integral gets simplified as

$$-\int \Psi^*\left[\frac{\partial}{\partial x}(V\Psi) - V\frac{\partial \Psi}{\partial x}\right]d\mathbf{r} = -\int \Psi^* \frac{\partial V}{\partial x}\Psi\, d\mathbf{r}$$

$$= -\left\langle \frac{\partial V}{\partial x}\right\rangle$$

[†] Green's second identity: If f and g are scalar functions of position, then

$$\int_V [f\,\nabla^2 g - g\,\nabla^2 f]\, d\mathbf{r} = \int_S [f\,\boldsymbol{\nabla} g - g\,\boldsymbol{\nabla} f]\cdot d\mathbf{S}$$

where V is the volume bounded by the closed surface S.

Thus,

$$\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

Similarly we can prove that

$$\frac{d}{dt}\langle p_y \rangle = -\left\langle \frac{\partial V}{\partial y} \right\rangle, \quad \frac{d}{dt}\langle p_z \rangle = -\left\langle \frac{\partial V}{\partial z} \right\rangle$$

These three equations are the three components of Equation (6.46). Thus, the proof of Ehrenfest's theorem is complete.

6.6 EXACT STATEMENT AND PROOF OF THE POSITION-MOMENTUM UNCERTAINTY RELATION

In order to have an exact statement and a mathematical proof of the uncertainty relation, we must first have a precise definition of uncertainty. It is simplest and most convenient to define *uncertainty* as the *root-mean-square deviation (also called the standard deviation) from the mean (i.e. the expectation) value*. Considering a wave packet moving along the x direction, we have

$$\Delta x = \left\langle (x - \langle x \rangle)^2 \right\rangle^{1/2}, \quad \Delta p = \left\langle (p - \langle p \rangle)^2 \right\rangle^{1/2} \tag{6.48}$$

Let us put

$$\left.\begin{aligned} A &= x - \langle x \rangle \\ \text{and} \qquad B &= p - \langle p \rangle = i\hbar\left[\frac{d}{dx} - \left\langle \frac{d}{dx} \right\rangle\right] \end{aligned}\right\} \tag{6.49}$$

Then

$$\begin{aligned} (\Delta x)^2 \ (\Delta p)^2 &= \int_{-\infty}^{\infty} \Psi^* \ A^2 \ \Psi dx \ \int_{-\infty}^{\infty} \Psi^* \ B^2 \Psi \ dx \\ &= \int_{-\infty}^{\infty} (A^* \Psi^*) \ (A\Psi) \ dx \ \int_{-\infty}^{\infty} (B^* \ \Psi^*) \ (B\Psi) dx \end{aligned} \tag{6.50}$$

The last step follows from the fact that A and B are Hermitian operators (see Equation 6.44). It can also be verified directly by partial integration and remembering that Ψ vanishes at infinity.

We shall use the *Schwarz inequality*

$$\int |f|^2 \ dx \ \int |g|^2 \ dx \geq \left| \int f^* g \, dx \right|^2 \tag{6.51}$$

where f and g are arbitrary functions and the equality is valid only if $f = \alpha g$, where α is a constant.

Taking $f = A\Psi$ and $g = B\Psi$, Equation (6.50) becomes

$$(\Delta x)^2(\Delta p)^2 \geq \left|\int (A^*\Psi^*)\,(B\Psi)\,dx\right|^2 = \left|\int \Psi^* AB\Psi\, dx\right|^2 \tag{6.52}$$

The expression on the right-hand side can be written as

$$\left|\int \Psi^*\left[\frac{1}{2}(AB - BA) + \frac{1}{2}(AB + BA)\right]\Psi dx\right|^2$$

$$= \frac{1}{4}\left|\int \Psi^*(AB - BA)\Psi\, dx\right|^2 + \frac{1}{4}\left|\int \Psi^*(AB + BA)\Psi\, dx\right|^2 \tag{6.53}$$

Here we have omitted the cross terms which can be shown to vanish by using the relation

$$\left[\int \Psi^* AB\Psi\, dx\right]^* = \int \Psi A^*\, B^*\, \Psi^*\, dx$$

$$= \int B^*\Psi^* A\Psi\, dx$$

$$= \int \Psi^*\, BA\, \Psi\, dx$$

Now from (6.49)

$$(AB - BA)\Psi = -i\hbar\left[x\frac{d\Psi}{dx} - \frac{d}{dx}(x\Psi)\right]$$

$$= -i\hbar\left[x\frac{d\Psi}{dx} - \Psi - x\frac{d\Psi}{dx}\right]$$

$$= i\hbar\,\Psi$$

Therefore,

$$\int \Psi^*(AB - BA)\Psi\, dx = i\hbar \int \Psi^*\,\Psi dx$$

$$= i\hbar \tag{6.54}$$

as Ψ is normalized.

From (6.52), (6.53) and (6.54) we obtain

$$(\Delta x)^2(\Delta p)^2 \geq \hbar^2/4$$

or

$$\boxed{\Delta x\,\Delta p \geq \hbar/2} \tag{6.55}$$

The equality can hold only if the second term on the right side of (6.53) is zero. Equation (6.55) is the exact statement of the position-momentum uncertainty relation, where the uncertainties in x and p are defined as root-mean-square deviations from the expectation values $\langle x \rangle$ and $\langle p \rangle$, respectively.

6.7 WAVE PACKET HAVING MINIMUM UNCERTAINTY PRODUCT

From the above derivation it is clear that the uncertainty product is minimum when the following two conditions are satisfied:

$$A\Psi = \alpha B\Psi \tag{6.56}$$

and $$\int \Psi^*(AB + BA)\Psi \, dx = 0 \tag{6.57}$$

Using Equation (6.49), Equation (6.56) gives

$$(x - \langle x \rangle)\Psi = \alpha\left[-i\hbar\frac{d\Psi}{dx} - \langle p \rangle \Psi\right]$$

Rearranging, we get the differential equation

$$\frac{d\Psi}{dx} = \left[\frac{i}{\alpha\hbar}\left(x - \langle x \rangle\right) + \frac{i}{\hbar}\langle p \rangle\right]\Psi$$

which on integration gives

$$\Psi(x) = N \exp\left[\frac{i}{2\alpha\hbar}\left(x - \langle x \rangle\right)^2 + \frac{i\langle p \rangle x}{\hbar}\right] \tag{6.58}$$

where N is an arbitrary constant.

Equation (6.57) gives

$$\int \Psi^* AB\Psi \, dx + \int B^*\Psi^* A\Psi \, dx = 0$$

Using (6.56), this becomes

$$\left(\frac{1}{\alpha} + \frac{1}{\alpha^*}\right)\int \Psi^* \, A^2 \, \Psi \, dx = 0$$

Since the integral is not zero, this yields

$$\frac{1}{\alpha} + \frac{1}{\alpha^*} = 0$$

which requires that α be purely imaginary. Further, since the integral of $|\Psi|^2$ should converge, α must be negative imaginary. In order to determine α, we require

$$\int \left(x - \langle x \rangle\right)^2 \, |\Psi|^2 \, dx = (\Delta x)^2$$

Evaluating the integral and substituting the value of α in (6.58), we obtain

$$\Psi(x) = N \exp\left[-\frac{\left(x - \langle x \rangle\right)^2}{4(\Delta x)^2} + \frac{i\langle p \rangle x}{\hbar}\right] \tag{6.59}$$

which is a gaussian function. Thus we find that *the wave packet having the minimum uncertainty product has a gaussian shape.*

6.8 THE TIME-INDEPENDENT SCHRÖDINGER EQUATION. STATIONARY STATES

There are many physically interesting problems in which the potential energy of the particle does not depend on the time, that is, $V = V(\mathbf{r})$. In such cases the

solution of the Schrödinger equation (6.16) gets considerably simplified because it is then possible to use the method of separation of variables. This method consists of assuming that the wave function $\Psi(\mathbf{r}, t)$ can be written as a product of two functions—a function of position only, $\psi(\mathbf{r})$, and a function of time only, $f(t)$:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\ f(t) \tag{6.60}$$

Then the Schrödinger Equation (6.16) becomes

$$i\hbar\ \psi(\mathbf{r})\frac{df(t)}{dt} = f(t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r})$$

Dividing both sides by $\psi(\mathbf{r})\ f(t)$, we get

$$i\hbar\ \frac{1}{f(t)}\frac{df(t)}{dt} = \frac{1}{\psi(\mathbf{r})}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r})$$

Note that the left-hand side depends only on t and right-hand side only on $\mathbf{r}$. Therefore, both sides must be equal to a constant. We shall denote this constant by E because, as we shall see shortly, this constant is equal to the energy of the particle, we thus obtain the two equations

$$\boxed{i\hbar\ \frac{df(t)}{dt} = E\ f(t)} \tag{6.61}$$

and

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\,\psi(\mathbf{r})} \tag{6.62}$$

The first of these equations depends only on the time t. It can be immediately integrated to give

$$f(t) = \exp\left(-\frac{iEt}{\hbar}\right) \tag{6.63}$$

The second equation depends only on the space coordinates. It is called the **time-independent Schrödinger equation**. The solution of this equation depends on the particular form of the potential $V(\mathbf{r})$. Once this is done, the full solution of the time-dependent Schrödinger equation (6.16) can be written as

$$\boxed{\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\exp(-iEt/\hbar)} \tag{6.64}$$

In the remaining part of this book, we shall be mainly concerned with the solution of the time-independent Schrödinger equation for simple systems. Therefore, let us look at this equation and some of its properties more deeply. We may write this equation as

$$\boxed{H\,\psi(\mathbf{r}) = E\,\psi(\mathbf{r})} \tag{6.65}$$

where H is the Hamiltonian operator

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \tag{6.66}$$

defined earlier in Equation (6.17).

Equation (6.65) has the following special property: The operator H acting on the function $\psi(\mathbf{r})$ gives back the function multiplied by the constant E. Such an equation is called an **eigenvalue equation**. The function ψ is called an **eigenfunction** of the operator H and E is the corresponding **eigenvalue**. In general many eigenfunctions and eigenvalues may correspond to a given H. The set of all the eigenvalues is called the *eigenvalue spectrum* of H. Since H is the Hamiltonian, the eigenvalues E are called the *energy eigenvalues* because these are the possible energies of the system. To indicate that an eigenfunction corresponds to a particular eigenvalue E_n, we put a subscript n with $\psi(\mathbf{r})$, that is, we write it as $\psi_n(\mathbf{r})$. The problem of solving the Schrödinger equation thus reduces to finding the eigenvalues and eigenfunctions of the Hamiltonian H.

Degeneracy

Sometimes it happens that more than one linearly independent eigenfunctions correspond to the same eigenvalue. The eigenvalue is then said to be *degenerate*. If there are k linearly independent eigenfunctions corresponding to the same eigenvalue, then this eigenvalue is said to be k-fold degenerate. It can be easily shown that *any linear combination of the degenerate eigenfunctions is also an eigenfunction corresponding to the same eigenvalue*. Thus, if $\psi_1, \psi_2, \ldots, \psi_k$ are linearly independent eigenfunctions corresponding to an eigenvalue E, then

$$\psi = c_1\psi_1 + c_2\psi_2 + \ldots + c_k\psi_k$$

is also an eigenfunction corresponding to E.

Reality of Eigenvalues

We shall now prove that all the energy eigenvalues are real and mention its consequences. Let E be the eigenvalue corresponding to the eigenfunction ψ. Then

$$H\psi = E\psi$$

Since the Hamiltonian H is a Hermitian operator, we have from Equation (6.31),

$$\int \psi^* H\psi \, d\mathbf{r} = \int (H\psi)^* \psi \, d\mathbf{r}$$

These equations give

$$\int \psi^* E\psi d\mathbf{r} = \int E^* \psi^* \psi d\mathbf{r}$$

or

$$(E - E^*) \int \psi^* \psi d\mathbf{r} = 0$$

Since the probability integral $\int \psi^* \psi d\mathbf{r}$ is necessarily positive, it follows that

$$E = E^*$$

Hence the eigenvalues of H are *real.*

Stationary States

An important consequence of the reality of eigenvalues is that the position probability density corresponding to the states represented by 'separable' wave functions (6.64) is independent of time:

$$\begin{aligned} P(\mathbf{r}, t) &= \Psi^*(\mathbf{r}, t)\ \Psi(\mathbf{r}, t) \\ &= \psi^*(\mathbf{r})\, e^{iEt/\hbar}\ \ \psi(\mathbf{r})\, e^{-iEt/\hbar} \\ &= \psi^*(\mathbf{r})\psi(\mathbf{r}) \end{aligned}$$

Therefore, these states are called *stationary states*. This name is further justified by the fact that the expectation value of the total energy operator in a state described by the wave function (6.64) is equal to the energy eigenvalue of that state for all time if the wave function is normalized:

$$\begin{aligned} &\int \Psi^*(\mathbf{r}, t) H \Psi(\mathbf{r}, t) d\mathbf{r} \\ &= \int \psi^*(\mathbf{r})\, e^{iEt/\hbar} H \psi(\mathbf{r})\, e^{-iEt/\hbar}\, d\mathbf{r} \\ &= \int \psi^*(\mathbf{r}) E \psi(\mathbf{r})\ d\mathbf{r} \\ &= E \int \psi^*(\mathbf{r}) \psi(\mathbf{r})\ d\mathbf{r} \\ &= E \end{aligned}$$

Orthogonality of Eigenfunctions

Another very important result is that the eigenfunctions corresponding to *distinct eigenvalues* are orthogonal. We prove it below.

Let ψ_k and ψ_n be the eigenfunctions corresponding to the eigenvalues E_k and E_n, respectively. Then

$$H\psi_k = E_k \psi_k \tag{6.67}$$

and

$$H\psi_n = E_n \psi_n \tag{6.68}$$

Taking complex-conjugate of (6.68) and remembering that E_n is real,

$$(H\psi_n)^* = E_n \psi_n^* \tag{6.69}$$

Premultiplying (6.67) by ψ_n^* and postmultiplying (6.69) by ψ_k, we obtain

$$\psi_n^* (H\psi_k) = E_k \psi_n^*\ \psi_k \tag{6.70}$$

and

$$(H\psi_n)^* \psi_k = E_n \psi_n^* \psi_k \tag{6.71}$$

Subtracting (6.71) from (6.78) and integrating, we obtain

$$(E_k - E_n)\int \psi_n^* \psi_k \, d\mathbf{r} = \int [\psi_n^*(H\psi_k) - (H\psi_n)^* \psi_k] d\mathbf{r}$$

Since H is Hermitian, the integral on the right-hand side is zero. Therefore,

$$(E_k - E_n)\int \psi_n^* \psi_k \, d\mathbf{r} = 0$$

Since $E_k \neq E_n$, this gives

$$\int \psi_k^* \psi_n \, d\mathbf{r} = 0$$

This shows that the eigenfunctions are orthogonal.

If an eigenvalue is degenerate, then the corresponding eigenfunctions are not necessarily orthogonal. However, it is always possible to construct a new set of mutually orthogonal eigenfunction using the *Schmidt orthogonalization procedure*. We shall not go into the details of this.[†]

If the eigenfunctions are normalized, then combining the normalization condition with the orthogonality condition, we have

$$\boxed{\int \psi_k^* \psi_n \, d\mathbf{r} = \delta_{kn}} \tag{6.72}$$

This equation is known as the **orthonormality condition**.

Parity

Before proceeding further, it is necessary to introduce the reader to the important concept of *parity*. For simplicity we shall discuss the one-dimensional case.

Suppose the potential function is symmetric about the origin, i.e., it is an even function:

$$V(x) = V(-x) \tag{6.73}$$

Let us study the behaviour of the Schrödinger equation under the operation of reflection through the origin, $x \to -x$. This operation is called the *parity operation*. The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\,\psi(x) \tag{6.74}$$

Replacing x by $-x$, we get

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x) = E\,\psi(-x) \tag{6.75}$$

where we have used (6.73). Comparing these equations we note that $\psi(x)$ and $\psi(-x)$ are eigenfunctions corresponding to the same eigenvalue E. There are two possible cases:

[†] For a discussion of this procedure, the student may consult Quantum Mechanics by E. Merzbacher, John Wiley, New York (1970).

Case 1: If the eigenvalue is **nondegenerate** then $\psi(x)$ and $\psi(-x)$ can differ only by a multiplicative constant:

$$\psi(-x) = c\psi(x)$$

Changing the sign of x in this equation, we get

$$\psi(x) = c\psi(-x)$$

Combining these two equations,

$$\psi(x) = c^2\psi(x)$$

so that $$c^2 = 1$$

or $$c = \pm 1$$

Therefore,

$$\psi(-x) = \pm\ \psi(x) \tag{6.76}$$

This shows that the eigenfunctions can be divided into two classes. The one for which

$$\psi(-x) = \psi(x) \tag{6.77}$$

are said to have **even parity**. The other, for which

$$\psi(-x) = -\psi(x) \tag{6.78}$$

are said to have **odd parity**.

Case 2: If the eigenvalue is **degenerate** then $\psi(-x)$ need not be a multiple of $\psi(x)$. In that case, $\psi(x)$ and $\psi(-x)$ are two linearly independent solutions corresponding to the same eigenvalue. Therefore, any linear combination of $\psi(x)$ and $\psi(-x)$ is also a possible eigenfunction. We can choose two linear combinations as

$$\psi_+(x) = \psi(x) + \psi(-x)$$

and $$\psi_-(x) = \psi(x) - \psi(-x)$$

Clearly $\psi_+(x)$ has **even** parity while $\psi_-(x)$ has **odd** parity.

Thus, we have proved that *for a symmetric potential, the eigenfunctions of the one-dimensional Schrödinger equation can always be chosen to have definite (even or odd) parity*. This fact often simplifies the calculation because we only have to find these eigenfunctions for positive values of x. Further, we know that even functions must have zero slope at the origin and odd functions vanish there. We shall illustrate these properties in our discussions of the square well and the harmonic oscillator.

Continuity and Boundary Conditions

In the next few chapters we shall be concerned with the solution of the Schrödinger equation to find the wave functions for various simple potentials. In order for a wave function to be physical acceptable, it must satisfy certain continuity and boundary conditions. We mention these below:

1. The Schrödinger equation (6.62) is a second-order differential equation. Therefore, if the potential energy $V(\mathbf{r})$ is finite, whether or not it is continuous, a knowledge of the wave function and its gradient along a surface is sufficient to solve the equation to obtain the wave function at any point. Thus, we impose the requirements that *the wave function and its gradient be single-valued, finite and continuous at every point in space*. These requirements ensure that a physical situation is represented uniquely by a wave function, and that the position probability density $P(\mathbf{r})$ and the probability current density $\mathbf{j}(\mathbf{r})$ are finite and continuous everywhere.
2. The wave functions are bounded at large distances in all directions.
3. If there is an infinite potential step at a surface, then the wave function at the surface is *zero* and the component of the gradient of the wave function normal to the surface is not determined.

In order to see why the wave function should be zero at an infinite potential step, let us solve the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

where $V(x) = 0$ for $x < 0$ and $V(x) = V_0$ for $x > 0$. We shall then pass to the limit $V_0 \to \infty$. Assuming that $V_0 > E \geq 0$, the general solution of the above equation are:

$$\text{For } x < 0: \qquad \psi(x) = A\sin kx + B\cos kx, \qquad k = \left[\frac{2mE}{\hbar^2}\right]^{1/2}$$

$$\text{For } x > 0: \qquad \psi(x) = Ce^{-Kx} + De^{Kx}, \qquad K = \left[\frac{2m}{\hbar^2}(V_0 - E)\right]^{1/2}$$

The boundary condition that ψ be bounded at large distance requires that $D = 0$. Then the continuity of ψ at $x = 0$ gives

$$B = C$$

and the continuity of $d\psi/dx$ gives

$$kA = -KC$$

Now K becomes infinite when V_0 does but the solution for $x < 0$ must be finite. Therefore, the second relation requires that C must become zero as $V_0 \to \infty$. Thus, when $V_0 \to \infty$, the wave function for $x \geq 0$ vanishes.

6.9 THE FREE PARTICLE

In section 6.2 we obtained the Schrödinger equation by assuming that a free particle can be represented by a plane wave. We shall now reverse the process and solve the Schrödinger equation for a free particle. For simplicity we shall consider one-dimensional case. The extension to three dimensions is straightforward.

The time-independent Schrödinger equation for a free particle is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

or
$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

or
$$\frac{d^2\psi}{dx^2} + k^2\psi = 0; \quad k = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \tag{6.79}$$

This equation has two linearly independent solutions, $\exp(ikx)$ and $\exp(-ikx)$. Therefore the general solution is

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{6.80}$$

where A and B are arbitrary constants. Clearly, for a solution to be physically acceptable, k must be real; otherwise $\psi(x)$ would become unbounded at one of the limits $x = \infty$ or $x = -\infty$. Therefore, we must have $E \geq 0$, that is, any non-negative value of energy is allowed. The energy spectrum is thus *continuous*.

The energy eigenvalues are given by

$$E = \frac{\hbar^2 k^2}{2m} \tag{6.81}$$

Each eigenvalue is doubly degenerate because two linearly independent eigenfunctions $\exp(ikx)$ and $\exp(-ikx)$ correspond to it.

Momentum Eigenfunctions

Let us now operate on the eigenfunctions $\exp(ikx)$ and $\exp(-ikx)$ with the momentum operator

$$p = -i\hbar\frac{d}{dx}$$

We have

$$-i\hbar\frac{d}{dx}(e^{ikx}) = \hbar k(e^{ikx}) \tag{6.82}$$

and

$$-i\hbar\frac{d}{dx}(e^{-ikx}) = -\hbar k\,(e^{-ikx}) \tag{6.83}$$

We find that the functions $\exp(ikx)$ and $\exp(-ikx)$ are eigenfunctions of the momentum operator with the eigenvalues $\hbar k$ and $-\hbar k$, respectively. Thus, these functions are not only energy eigenfunctions, but also *momentum eigenfunctions*.

Physical Interpretation of the Wave Functions

Following Equation (6.64), the full wave function for a free particle can be written as

$$\begin{aligned}\Psi(x, t) &= (Ae^{ikx} + Be^{-ikx})\,e^{-iEt/\hbar} \\ &= Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)}\end{aligned} \tag{6.84}$$

where $\omega = E/\hbar$ is the angular frequency. Let us now consider the case when $B = 0$. The resulting wave function is

$$\Psi(x, t) = Ae^{i(kx - \omega t)} \tag{6.85}$$

This is a plane wave travelling in the positive x-direction. Therefore, it must be associated with a free particle of mass m moving along the x-axis in the positive direction with momentum $p = \hbar k$ and energy $E = \hbar^2 k^2/2m$.

The **position probability density** corresponding to the wave (6.85) is

$$P = |\Psi(x, t)|^2 = |A|^2 \tag{6.86}$$

We find that P is independent of time t as well as the position x of the particle. Thus the position of a particle represented by a plane wave is completely unknown. This is in accordance with the uncertainty relation (5.28) because if a particle has precisely defined momentum, then $\Delta p = 0$ and therefore, $\Delta x = \infty$. Therefore, *a plane wave may be physically interpreted as representing a particle of well-defined momentum moving in a beam of unlimited length.*

The **probability current density** corresponding to the wave (6.85) is given by (see Equation 6.33)

$$\begin{aligned} j &= \text{Re}\left[\psi^* \frac{\hbar}{im} \frac{\partial \psi}{\partial x}\right] \\ &= \text{Re}\left[A^* e^{-ikx} \left(\frac{\hbar}{im}\right)(ik)\, Ae^{ikx}\right] \\ &= \frac{\hbar k}{m}|A|^2 = \frac{p}{m}|A|^2 = vP \end{aligned} \tag{6.87}$$

This is independent of t and x, as expected for stationary states. The relation $j = vP$ is analogous to the well known relation between flux, velocity and density in hydrodynamics.

In (6.84), if we set $A = 0$, the resulting wave function would be

$$\Psi(x, t) = Be^{-i(kx + \omega t)} \tag{6.88}$$

This represents a plane wave travelling in the negative x-direction. The corresponding position probability density and probability current density are, respectively,

$$P = |B|^2 \tag{6.89}$$

and

$$j = -v|B|^2 = -vP \tag{6.90}$$

Normalization of Momentum Eigenfunctions

Let us consider the momentum eigenfunction

$$\psi_k(x) = Ae^{ikx} \tag{6.91}$$

It is easy to see that $\psi(x)$ cannot be normalized in the usual sense because the integral $\int_{-\infty}^{\infty} |\psi_k(x)|^2\, dx$ is infinite. Therefore, if these wave functions are to be used in practical situations, it is necessary to have alternative ways of normalizing them. There are two methods of normalizing these functions, which are briefly described below.

Box Normalization

It is assumed that the particle is enclosed in a large one-dimensional box of length L, at the walls of which the wave functions satisfy periodic boundary condition

$$\psi_k(x + L) = \psi_k(x)$$

or $$e^{ik(x+L)} = e^{ikx}$$

or $$e^{ikL} = 1$$

This restricts k to the discrete values

$$k = \frac{2\pi n}{L}, \quad n = 0, \pm 1, \pm 2, \ldots \tag{6.92}$$

Therefore, the energy levels also become discrete:

$$E_n = \frac{2\pi^2 \hbar^2 n^2}{mL^2} \tag{6.93}$$

As L increases, the spacings of the energy levels decreases. So for a very large box, the energy level spectrum is practically continuous. The normalization of $\psi_k(x)$ is achieved by requiring that

$$\int_{-L/2}^{L/2} |\psi_k(x)|^2\, dx = 1 \tag{6.94}$$

which gives $|A|^2 = 1/L$. Taking the phase of the constant A to be zero, we have $A = L^{-1/2}$. Therefore, the *normalized momentum eigenfunctions* are given by

$$\boxed{\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}} \tag{6.95}$$

The eigenfunctions are, in fact, **orthonormal**:

$$\int_{-L/2}^{L/2} \psi_{k'}^*(x)\psi_k(x)dx = \frac{1}{L}\int_{-L/2}^{L/2} e^{i(k-k')x}\, dx = \delta_{kk'} \tag{6.96}$$

Delta-function Normalization

The box normalization has the shortcoming that it converts the continuous set of momentum eigenfunctions into a discrete set. Another method of normalization, which avoids this difficulty, is by using the Dirac delta-function, defined in Appendix B. Using Equation (B.11), we have

$$\int_{-\infty}^{\infty} e^{i(k-k')x}\,dx = 2\pi\delta(k-k') \tag{6.97}$$

Thus, the *normalized momentum eigenfunctions* can be written as

$$\boxed{\psi_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}} \tag{6.98}$$

These functions satisfy the **orthonormality condition**

$$\int_{-\infty}^{\infty} \psi_{k'}^*(x)\ \psi_k(x)dx = \delta(k - k') \tag{6.99}$$

SUMMARY

1. The wave function $\Psi(\mathbf{r}, t)$ for a physical system at any point $(\mathbf{r}, t)$ in space and time satisfies the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right)\Psi(\mathbf{r}, t)$$

where $V(\mathbf{r}, t)$ is the potential energy of the particle. The operator on the right is called the Hamiltonian operator and is denoted by the symbol H:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)$$

The Schrödinger equation is linear and homogeneous, so that the superposition principal holds. It is consistent with the relations $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$.

2. The Schrödinger equation is, in a sense, the quantum mechanical 'translation' of the classical equation $E = p^2/2m$, where the energy E and the momentum $\mathbf{p}$ are represented by differential operators

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

and

$$\hat{\mathbf{p}} = -i\hbar\nabla$$

respectively, acting on the wave function $\Psi(\mathbf{r}, t)$.

3. The wave function has a statistical interpretation: If a particle is described by a wave function $\Psi(\mathbf{r}, t)$, then the quantity

$$P(\mathbf{r}, t) = \Psi^*\Psi = |\Psi|^2$$

is called the position probability density. Since the probability of finding the particle somewhere at time t is unity, the wave function is chosen to satisfy the normalization condition

$$\int \Psi^*\Psi\, d\mathbf{r} = 1$$

where the integral extends over all space.

4. The vector

$$\mathbf{j}(\mathbf{r}, t) = \frac{\hbar}{2im}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) = \mathrm{Re}\left[\Psi^* \frac{\hbar}{im}\nabla\Psi\right]$$

is called the probability current density. P and $\mathbf{j}$ are related through the equation of continuity

$$\frac{\partial P}{\partial t} + \nabla\cdot\mathbf{j} = 0$$

If $\nabla\cdot\mathbf{j}$ is zero in a state, then for that state the probability density is constant in time. Such states are called stationary states.
If $\mathbf{v}$ is the velocity of the particle, then

$$\mathbf{j} = P\mathbf{v}$$

5. The expectation value of a dynamical quantity $A(\mathbf{r}, \mathbf{p}, t)$, associated with a particle in a state $\Psi(\mathbf{r}, t)$, is given by

$$\langle A\rangle = \int \Psi^*(\mathbf{r}, t)\ \hat{A}(\mathbf{r}, -i\hbar\nabla, t)\ \Psi(\mathbf{r}, t)\ d\mathbf{r}$$

6. The operator $\hat{A}$ associated with a physical quantity A is always Hermitian, i.e.,

$$\int \Psi^*\hat{A}\Psi d\mathbf{r} = \int (\hat{A}\Psi)^*\Psi\, d\mathbf{r}$$

This ensures that the expectation value of A is real.

7. According to Ehrenfest's theorem, the equations of motion of the expectation values of the position and momentum vectors for a wave packet are formally identical to Newton's equations:

$$\frac{d}{dt}\langle\mathbf{r}\rangle = \frac{\langle\mathbf{p}\rangle}{m}$$

and

$$\frac{d}{dt}\langle\mathbf{p}\rangle = -\langle\nabla V\rangle$$

8. In order to have an exact statement of the position-momentum uncertainty relation, it is convenient to define the uncertainty as the root-mean-square deviation from the expectation value. Considering a wave packet moving in the x-direction,

$$\Delta x = \langle(x - \langle x\rangle)^2\rangle^{1/2},\ \Delta p = \langle(p - \langle p\rangle)^2\rangle^{1/2}$$

The uncertainty relation then becomes

$$\Delta x\Delta p \geq \hbar/2$$

9. The wave packet having the minimum uncertainty product has a gaussian shape.

10. If the potential energy of the particle does not depend on the time, then the wave function can be written as

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\ f(t)$$

The function $f(t)$ is given by

$$f(t) = \exp\left(-\frac{iEt}{\hbar}\right)$$

The function $\psi(\mathbf{r})$ depends on the potential $V(\mathbf{r})$ and is obtained by solving the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Such an equation is called an eigenvalue equation. The function ψ is called an eigenfunction and E is the corresponding eigenvalue of the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

In general, many eigenfunctions and eigenvalues correspond to a given H. The eigenvalues are the possible energies of the system.

11. If there are k linearly independent eigenfunctions corresponding to the same eigenvalue, then this eigenvalue is said to be k-fold degenerate. Any linear combination of the degenerate eigenfunctions is also an eigenfunction corresponding to the same eigenvalue.

12. The energy eigenvalues are real. An important consequence of this fact is that the position probability density of a state is independent of time. Therefore, these states are called stationary states.

13. The eigenfunctions corresponding to distinct eigenvalues are orthogonal. If the eigenvalues are not distinct, then also it is possible to construct a set of orthogonal eigenfunctions using the Schmidt orthogonalization procedure. Thus, the eigenfunctions can always be chosen to satisfy the orthonormality condition

$$\int \psi_k^* \, \psi_n \, d\mathbf{r} = \delta_{kn}$$

14. If the potential function is symmetric about the origin, the eigenfunctions can always be chosen to have definite (even or odd) parity.

15. A physically acceptable wave function and its gradient must be single-valued, finite and continuous at every point and must be bounded at large distances. Further, the wave function must vanish at an infinite potential step.

16. The time-independent Schrödinger equation for a free particle in one dimension is

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0;\ k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

Its solutions $\exp(\pm ikx)$ are not only energy eigenfunctions but also momentum eigenfunctions.

17. The momentum eigenfunctions may be normalized either by using box normalization or by using the Dirac delta-function.

18. A plane wave

$$\Psi(x, t) = Ae^{i(kx-\omega t)}$$

may be physically interpreted as representing a particle of well-defined momentum moving in a beam of unlimited length.

QUESTIONS

1. Write the time-dependent Schrödinger equation for a particle of mass m moving under a force which is derivable from a potential $V(\mathbf{r}, t)$. What is the physical interpretation of the wave function? Why should the wave function be normalized?

2. Show that the normalization integral is independent of time.

3. What is the Hamiltonian operator? Show that the conservation of probability implies that the Hamiltonian is an Hermitian operator.

4. Define the position probability density and the probability current density in the context of a quantum mechanical wave function. Obtain the equation connecting these quantities and give the physical interpretation of this equation.

5. If the functions Ψ_1 and Ψ_2 are solutions of the Schrödinger equation for a particle, then show that $a_1\Psi_1 + a_2\Psi_2$, where a_1 and a_2 are arbitrary constants, is also a solution of the same equation.

6. (a) What is meant by the expectation value of a dynamical variable? How is it obtained mathematically?

(b) Show that the expectation value of a physical quantity can be real only if the corresponding operator is Hermitian.

(c) Show by actual integration that $\langle p_x \rangle$ is real.

7. State and prove Ehrenfest's theorem.

8. Defining uncertainty in a suitable manner, give the exact statement and proof of the position-momentum uncertainty relation.

9. Show that the wave packet having the minimum uncertainty product has a gaussian shape.

10. Consider a particle moving in a potential which is independent of time. Assuming that its wave function can be written as $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, f(t)$, obtain the equations satisfied by $\psi(\mathbf{r})$ and $f(t)$. Which of these equations is called the time-independent Schrödinger equation?

11. Show that the eigenvalues of the time-independent Schrödinger equation $H\psi = E\psi$ are real.

12. What are stationary states? Show that the probability current density is divergenceless for such states.

13. Show that the eigenfunctions corresponding to distinct eigenvalues of the Hamiltonian are orthogonal.

14. Show that for a symmetric potential, the eigenfunctions of the time-independent Schrödinger equation can be chosen to have definite parity.

15. What are the continuity and boundary conditions that must be satisfied for a wave function to be physically acceptable?

16. What are momentum eigenfunctions? Discuss the methods of normalizing these functions.

Chapter

7

Particle in a Potential Well

Chapter Contents

7.1 One-Dimensional Infinite Square Well
7.2 Three-Dimensional Infinite Square Well
7.3 One-Dimensional Finite Square Well (First Type)
7.4 One-Dimensional Finite Square Well (Second Type)

In section 6.9 we solved the Schrödinger equation for a free particle. As expected, the eigenfunctions are plane waves and the energy spectrum is continuous, ranging from $E = 0$ to $E = +\infty$. We shall now study the motion of a particle which is confined in a region of constant potential energy (which is taken to be zero). There are two possibilities: (i) the region may be bounded by perfectly rigid walls which corresponds to infinite potential, and (ii) the region may be bounded by finite potential steps.

Because of their appearance, the systems are generally called *square* (or *rectangular*) *wells*. A square well is the simplest type of bound system. With modern techniques involving semiconductors, potentials very close to this simple version can be produced.

For the infinite well we shall discuss both the one-dimensional and three-dimensional cases while for the finite well only the one-dimensional case will be discussed.

We shall see that the confinement of a particle in a limited region leads to *quantization* of energy.

7.1 ONE-DIMENSIONAL INFINITE SQUARE WELL

Let us consider a particle of mass m confined in a region of width $2a$ from $x = -a$ to $x = +a$ by impenetrable walls. Such a system is also called a **one-**

dimensional box. Inside the box the particle is free but experiences a sudden large force directed towards the origin as it reaches the points $x = \pm a$. Therefore, the potential energy for this problem is,

$$V(x) = \begin{cases} 0 & |x| < a \\ \infty & |x| > a \end{cases} \tag{7.1}$$

The potential is shown in Figure 7.1.

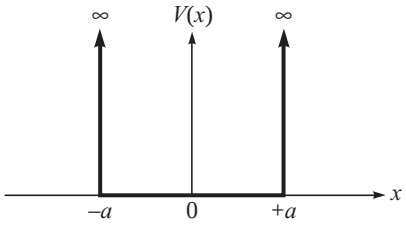

Figure 7.1 The one-dimensional infinite square well potential.

In order to find the eigenfunctions and energy eigenvalues for this system, we have to solve the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\,\psi(x) \tag{7.2}$$

Since the potential energy is infinite at $x = \pm a$, the probability of finding the particle outside the well is zero. Therefore the wave function $\psi(x)$ must vanish for $|x| > a$. Further, since the wave function must be continuous, it must vanish at the walls:

$$\psi(x) = 0 \qquad \text{at} \qquad x = \pm a \tag{7.3}$$

For $|x| < a$, the Schrödinger equation (7.2) reduces to

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0; \quad k^2 = \frac{2mE}{\hbar^2} \tag{7.4}$$

The general solution[†] of this equation is

$$\psi(x) = A \sin kx + B \cos kx \tag{7.5}$$

Applying the boundary condition (7.3), we obtain at $x = a$,

$$A \sin ka + B \cos ka = 0$$

and at $x = -a$,

$$-A \sin ka + B \cos ka = 0$$

These equations give

$$A \sin ka = 0, \quad B \cos ka = 0 \tag{7.6}$$

[†] The general solution can also be written in the complex form: $\psi = A\exp(ikx) + B\exp(-ikx)$. However, in the present problem it is more convenient to use the real form (7.5).

Now we cannot allow both A and B to be zero because this would give the physically uninteresting trivial solution $\psi(x) = 0$ for all x. Also, we cannot make both $\sin ka$ and $\cos ka$ zero for a given value of k. Hence, there are *two* possible classes of solutions:

For the *first* class,

$$A = 0 \quad \text{and} \quad \cos ka = 0$$

and for the *second* class,

$$B = 0 \quad \text{and} \quad \sin ka = 0$$

These conditions are satisfied if

$$ka = \frac{n\pi}{2} \tag{7.7}$$

where n is an *odd* integer for the first class and an *even* integer for the second class. Thus, the eigenfunctions for the two classes are, respectively,

$$\boxed{\psi_n(x) = B \cos \frac{n\pi x}{2a}, \quad n = 1,3,5,\ldots}$$

and

$$\boxed{\psi_n(x) = A \sin \frac{n\pi x}{2a}, \quad n = 2,4,6,\ldots}$$

In order to normalize the eigenfunctions, we apply the condition

$$\int_{-a}^{a} \psi_n^*(x)\ \psi_n(x)dx = 1$$

This gives

$$A^2 \int_{-a}^{a} \sin^2 \frac{n\pi x}{2a}\, dx = B^2 \int_{-a}^{a} \cos^2 \frac{n\pi x}{2a}\, dx = 1$$

Solving these integrals we obtain

$$\boxed{A = B = 1/\sqrt{a}} \tag{7.8}$$

Thus, the **normalized eigenfunctions** for the two classes are, respectively,

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{a}} \cos \frac{n\pi x}{2a}, \quad n = 1,3,5,\ldots} \tag{7.9}$$

and

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{a}} \sin \frac{n\pi x}{2a}, \quad n = 2,4,6,\ldots} \tag{7.10}$$

It may be noted that it is unnecessary to consider negative values of n because the resulting solutions will not be linearly independent of those corresponding to positive values of n.

From (7.7), the only allowed values of k are

$$k_n = \frac{n\pi}{2a}, \quad n = 1,2,3,\ldots \tag{7.11}$$

Using (7.4) and (7.11) the **energy eigenvalues** for both the classes are given by

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{8ma^2}, \qquad n = 1,2,3,\ldots} \tag{7.12}$$

Thus, the energy is *quantized*. The integer n is called a *quantum number*. There is an *infinite* sequence of *discrete energy levels*. There is only one eigenfunction for each level, so the energy levels are *nondegenerate*.

It can be easily shown that the eigenfunctions $\psi_m(x)$ and $\psi_n(x)$ corresponding to different eigenvalues are orthogonal:

$$\int_{-a}^{a} \psi_m^*(x)\,\psi_n(x)\,dx = 0, \quad m \neq n$$

Combining orthogonality and normalization, we have the *orthonormality* condition:

$$\int_{-a}^{a} \psi_m^*(x)\,\psi_n(x)\,dx = \delta mn \tag{7.13}$$

The first four energy levels, eigenfunctions and position probability densities are shown in Figures 7.2, 7.3 and 7.4, respectively.

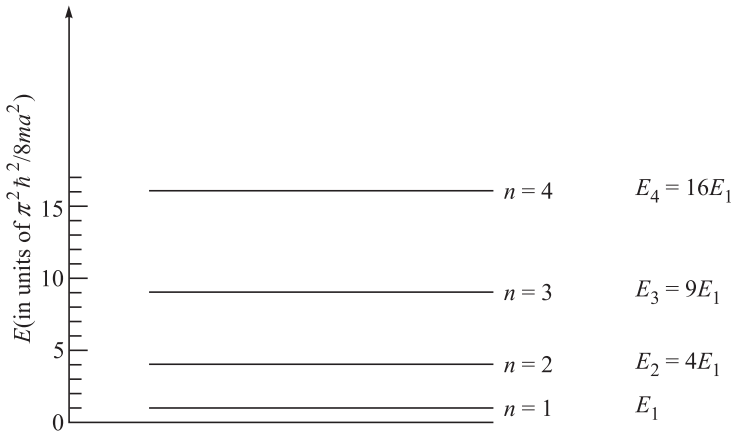

Figure 7.2 Energy-level diagram.

Connection with the De Broglie Hypothesis

It is interesting to note the connection between the eigenfunctions of the infinite square well and the de Broglie hypothesis. The de Broglie wavelength for the nth quantum state is

$$\lambda_n = \frac{2\pi}{k_n} = \frac{2}{n}(2a)$$

This gives

$$2a = \frac{n}{2}\lambda_n$$

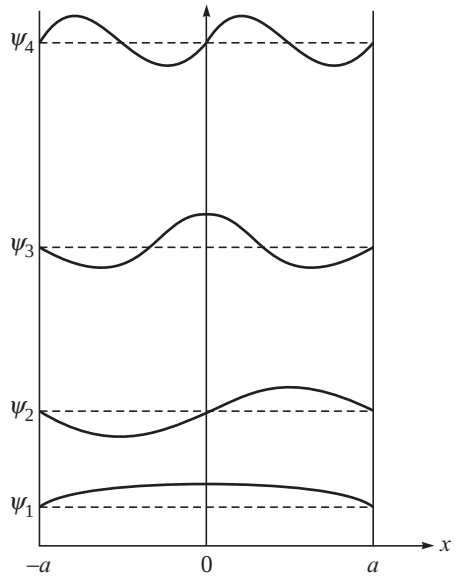

Figure 7.3 Wave functions.

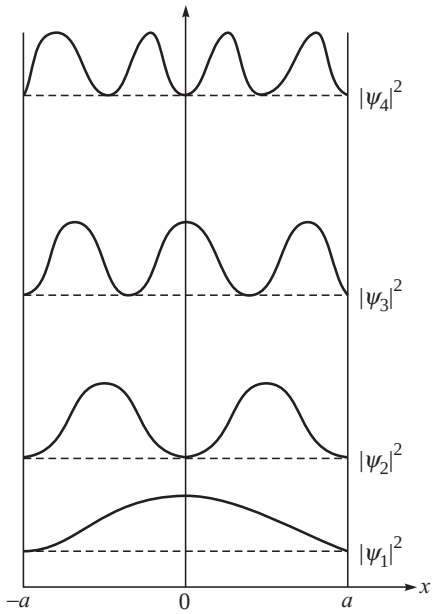

Figure 7.4 Probability densities.

This shows that *the n*th *quantum state is obtained when n*/2 *de Broglie wavelengths can fit into the box.*

Also note that the *n*th eigenfunction has $(n - 1)$ nodes within the box. This follows from (7.9) and (7.10).

Zero-point Energy

It is important to note that the lowest possible energy, also called the *zero-point energy*, is not zero. This fact is in agreement with the *uncertainty principle*. By trapping the particle in a limited region, we acquire information about its position. Therefore, its momentum cannot be known with complete precision. This prevents any possibility of the particle being at rest. Hence the lowest energy cannot be zero.

The position uncertainty is roughly given by $\Delta x \approx a$. Therefore the minimum momentum uncertainty is $\Delta p \approx \hbar/a$. This leads to a minimum kinetic energy of order $\hbar^2/ma^2$. Equation (7.12) tells us that this agrees, qualitatively, with the value of E_1.

Parity

The two classes of eigenfunctions that we have obtained have one important difference. The eigenfunctions (7.9) belonging to the *first class* are even functions of x:

$$\psi_n(-x) = \psi_n(x)$$

These functions are said to have *even parity*. On the other hand, the eigenfunctions (7.10) belonging to the *second class* are odd functions of x:

$$\psi_n(-x) = -\psi_n(x)$$

These functions are said to have *odd parity*. As discussed in section 6.8, this division of the eigenfunctions into even and odd types is a consequence of the fact that the potential is symmetric about the origin: $V(-x) = V(x)$.

PROBLEM 7.1 Calculate (*a*)$\langle x \rangle$, (*b*) $\langle p \rangle$, (c) $\langle x^2 \rangle$ and (*d*) $\langle p^2 \rangle$ for a particle in a one-dimensional box shown in Figure 7.1.

Solution: We shall consider the even parity wave functions

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos kx, \quad k = \frac{n\pi}{2a}, \quad n = 1, 3, 5,\ldots$$

The same results are obtained if we consider the odd parity wave functions.

(a) $$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^* x \, \psi_n \, dx$$

$$= \frac{1}{a} \int_{-a}^{a} x \cos^2 kx \, dx$$

$$= 0, \text{ since the integrand is odd.}$$

This result is as expected; the probability density $\psi^*\psi$ is symmetric about $x = 0$, indicating that the particle spends as much time to the left of the centre as to the right.

(b) $$\langle p \rangle = \int_{-\infty}^{\infty} \psi_n^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi_n \, dx$$

$$= -\frac{i\hbar}{a} \int_{-a}^{a} \cos kx \, (-k \sin kx) dx$$

$$= \frac{i\hbar k}{a} \int_{-a}^{a} \cos kx \sin kx \, dx$$

$$= 0, \text{ since the integrand is odd.}$$

Again, the result is as expected. The particle moves back and forth, spending half its time moving towards the left and half its time moving towards the right. Thus the average momentum must be zero.

(c) $$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* \, x^2 \, \psi_n \, dx$$

$$= \frac{1}{a} \int_{-a}^{a} x^2 \cos^2 kx \, dx$$

$$= \frac{2}{2a} \int_{0}^{a} x^2 (1 + \cos 2kx) dx$$

$$= \frac{1}{a} \left[\frac{x^3}{3}\right]_0^a + \frac{1}{a} \int_0^a x^2 \cos (2kx) dx$$

$$= \frac{a^2}{3} + \frac{1}{a}\int_0^a x^2 \cos(2kx)\, dx$$

Integrating by parts

$$\int_0^a x^2 \cos(2kx)\, dx = \frac{1}{2k}\left[x^2 \sin 2kx\right]_0^a - \frac{1}{k}\int_0^a x \sin(2kx)\, dx$$

The first term vanishes since $2ka = n\pi$ and $\sin n\pi = 0$. The integral in the second term gives

$$\int_0^a x \sin(2kx)\, dx = -\frac{1}{2k}\left[x \cos 2kx\right]_0^a + \frac{1}{2k}\int_0^a \cos(2kx)\, dx$$

$$= \frac{a}{2k} + \frac{1}{4k^2}\left[\sin 2kx\right]_0^a = \frac{a}{2k}$$

The first term has been evaluated using $\cos n\pi = -1$ as n is odd. Thus, we obtain

$$\langle x^2 \rangle = \frac{a^2}{3} + \left(\frac{1}{a}\right)\left(-\frac{1}{k}\right)\left(\frac{a}{2k}\right)$$

$$= \frac{a^2}{3} - \frac{1}{2k^2}$$

$$= \frac{a^2}{3} - \frac{1}{2}\left(\frac{2a}{n\pi}\right)^2$$

$$= \frac{a^2}{3} - \frac{2a^2}{n^2\pi^2}$$

$$= a^2\left(\frac{1}{3} - \frac{2}{n^2\pi^2}\right)$$

(d)
$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* p^2 \psi_n\, dx$$

$$= \frac{1}{a}\int_{-a}^{a} \cos(kx)\left(-\hbar^2 \frac{d^2}{dx^2}\right) \cos(kx)\, dx$$

$$= \frac{\hbar^2 k^2}{a}\int_{-a}^{a} \cos^2 kx\, dx$$

$$= \frac{2\hbar^2 k^2}{2a}\int_0^a (1 + \cos(2kx))\, dx$$

$$= \frac{2\hbar^2 k^2}{2a}\left[[x]_0^a + \int_0^a \cos(2kx)\, dx\right]$$

$$= \hbar^2 k^2 = \frac{n^2\pi^2\hbar^2}{4a^2}$$

PROBLEM 7.2 Show that the uncertainty relation $\Delta x\, \Delta p \geq \hbar/2$ is satisfied in the case of a particle in a one-dimensional box.

Solution: From section 6.6, the uncertainty Δx in x is defined as

$$\begin{aligned}(\Delta x)^2 &= \langle (x - \langle x \rangle)^2 \rangle \\ &= \langle x^2 - 2x \langle x \rangle + \langle x \rangle^2 \rangle \\ &= \langle x^2 \rangle - \langle x \rangle^2\end{aligned}$$

Similarly, the uncertainty Δp in p is defined as

$$(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2$$

Using Problem 7.1,

$$(\Delta x)^2 = a^2\left(\frac{1}{3} - \frac{2}{n^2\pi^2}\right)$$

and

$$(\Delta p)^2 = \frac{n^2\pi^2\hbar^2}{4a^2}$$

Therefore,

$$(\Delta x)^2(\Delta p)^2 = n^2\pi^2\hbar^2\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)$$

or

$$\Delta x\ \Delta p = \hbar\left(\frac{\pi^2 n^2}{12} - \frac{1}{2}\right)^{1/2}$$

The smallest value of this uncertainty product is for the ground state ($n = 1$). We get on simplifying

$$(\Delta x\ \Delta p)_{n=1} = 0.567\hbar$$

This is in agreement with

$$\Delta x \Delta p \geq \hbar/2$$

PROBLEM 7.3 Consider a particle of mass m, moving in a one-dimensional infinite square well of width L, such that the left corner of the well is at the origin. Obtain the energy eigenvalues and the corresponding normalized eigenfunctions of the particle.

Solution: This is an **alternate version** of the infinite square well problem. The students must learn to solve it and compare the eigenvalues and eigenfunctions with those obtained in section 7.1.

The potential energy is

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x < 0 \quad \text{and} \quad x > L \end{cases} \tag{7.14}$$

Thus, we have to solve the Schrödinger equation (7.4) subject to the boundary conditions

$$\psi(0) = \psi(L) = 0 \tag{7.15}$$

The general solution is again given by (7.5). The boundary condition at $x = 0$ requires that $B = 0$. The boundary condition at $x = L$ requires that

$$kL = n\pi, \qquad n = 1, 2, 3\ldots$$

Thus the eigenvalues are

$$\boxed{E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad n = 1,2,3,\ldots} \tag{7.16}$$

and the corresponding eigenfunctions are

$$\psi(x) = A \sin\left(\frac{n\pi x}{L}\right), \qquad n = 1,2,3,$$

The normalization condition requires

$$\boxed{A = \sqrt{\frac{2}{L}}}$$

Therefore, the normalized eigenfunctions are

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \qquad n = 1,2,3,\ldots} \tag{7.17}$$

Note that the energies of the particle are same as in Equation (7.12) because $L = 2a$.

PROBLEM 7.4 Calculate the three lowest energy levels (in eV) for an electron inside a one-dimensional infinite potential well of width 2 Å. Also determine the corresponding normalized eigenfunctions. Given mass of electron $m = 9.1 \times 10^{-31}$ kg, $\hbar = 1.05 \times 10^{-34}$Js, 1 eV $= 1.6 \times 10^{-19}$ J.

Solution: **Energies**

If the width of the well is $2a$ from $-a < x < a$, then the energy of the nth level is given by

$$E_n = \frac{n^2\pi^2\hbar^2}{8ma^2}$$

Here $a = 1\text{Å} = 10^{-10}$m. The three lowest levels correspond to $n = 1, 2, 3$. We have

$$E_1 = \frac{(3.14)^2 \times (1.05 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (10^{-10})^2}$$

$$= 14.93 \times 10^{-19} \text{ J}$$

$$= \boxed{9.3 \text{ eV}}$$

$$E_2 = 4E_1 = \boxed{37.2 \text{ eV}}$$

$$E_3 = 9E_1 = \boxed{83.7 \text{ eV}}$$

Eigenfunctions

$$\psi_1(x) = \frac{1}{\sqrt{a}} \cos \frac{\pi x}{2a}$$

$$= \frac{1}{10^{-5}} \cos\left(\frac{\pi x}{2 \times 10^{-10}}\right)$$

$$\psi_2(x) = \frac{1}{10^{-5}} \sin\left(\frac{2\pi x}{2 \times 10^{-10}}\right)$$

$$= \frac{1}{10^{-5}} \sin\left(\frac{\pi x}{10^{-10}}\right)$$

$$\psi_3(x) = \frac{1}{10^{-5}} \cos\left(\frac{3\pi x}{2 \times 10^{-10}}\right)$$

PROBLEM 7.5 Can we measure the energy levels of a ball of mass 10 g moving in a one-dimensional box of length 10 cm?

Solution: The energy levels of a particle of mass m in a box of length L is given by

$$E_n = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$$

Substituting the values

$$E_n = \frac{(3.14)^2 (1.054 \times 10^{-34})^2 n^2}{2 \times (10 \times 10^{-3}) (10 \times 10^{-2})^2}$$

$$= 5.2 \times 10^{-64} n^2 \text{ J}$$

$$= 3.25 \times 10^{-45} n^2 \text{ eV}$$

Taking $n = 1, 2, 3, \ldots$

$E_1 = 3.25 \times 10^{-45}$ eV

$E_2 = 13 \times 10^{-45}$ eV

$E_3 = 29.25 \times 10^{-45}$ eV

etc. These energies are extremely small and close together and hence **cannot** be measured.

PROBLEM 7.6 Obtain an expression for the wavelength of the photon emitted when a particle of mass m in an infinite well of width $2a$ makes a transition from a higher state of quantum number n_2 to a lower state of quantum number n_1.

Solution: The frequency of the emitted photon is

$$\nu = \frac{E_{n_2} - E_{n_1}}{h} \tag{7.18}$$

Therefore, the wavelength of the photon is

$$\lambda = \frac{c}{\nu} = \frac{ch}{E_{n_2} - E_{n_1}} = \frac{2\pi c\hbar}{E_{n_2} - E_{n_1}} \tag{7.19}$$

Now

$$E_{n_2} = \frac{n_2^2 \pi^2 \hbar^2}{8ma^2}$$

and

$$E_{n_1} = \frac{n_1^2 \pi^2 \hbar^2}{8ma^2}$$

Therefore

$$E_{n_2} - E_{n_1} = \frac{(n_2^2 - n_1^2)\,\pi^2 \hbar^2}{8ma^2} \tag{7.20}$$

Substituting in (7.19)

$$\lambda = \frac{(2\pi c\hbar)\,(8ma^2)}{(n_2^2 - n_1^2)\pi^2 \hbar^2}$$

or

$$\lambda = \boxed{\frac{16\,cma^2}{(n_2^2 - n_1^2)\pi\hbar}} \tag{7.21}$$

Note: For a well of width L, we have

$$\lambda = \boxed{\frac{4\,cmL^2}{(n_2^2 - n_1^2)\pi\hbar}} \tag{7.22}$$

PROBLEM 7.7 A beam of photons in a range of wavelengths $\lambda = 9.0 \pm 1.0$ nm strikes an electron in an infinite well of width 1.0 nm. The electron is in the ground state. To what higher states can the electron be excited?

Solution: If the electron is excited to the nth state, then using Equation (7.22),

$$n^2 - 1 = \frac{4\,cmL^2}{\lambda\pi\hbar}$$

$$= \frac{4 \times 3 \times 10^8 \times 9.1 \times 10^{-31} \times (10^{-9})^2}{(9.0 \pm 1.0) \times 10^{-9} \times 3.14 \times 1.054 \times 10^{-34}}$$

Solving this equation, we find that $n \approx 20$ when plus sign is taken in the denominator and $n \approx 18$ when minus sign is taken. Thus, the possible values of n are **18, 19 and 20**.

PROBLEM 7.8 Calculate the probability that a particle in a one-dimensional box of length L can be found between 0.4 L to 0.6 L for the (a) ground state, (b) first excited state, (c) second excited state.

Solution: The wave function for a particle in the nth state is given by Equation (7.17):

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L}$$

The probability of finding the particle in an interval of width dx about a point x is

$$P_n(x)dx = \psi_n^*(x)\psi_n(x)dx$$
$$= \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)dx$$

Here $$dx = (0.6 - 0.4)L = 0.2L$$

and $$x = \left(\frac{0.4 + 0.6}{2}\right)L = \frac{L}{2}$$

For the ground state, $n = 1$. Therefore,

$$P_1 dx = \frac{2}{L}\sin^2\left(\frac{\pi}{L}\cdot\frac{L}{2}\right) \times 0.2L = \boxed{0.4}$$

For the first excited state, $n = 2$. Therefore,

$$P_2 dx = \frac{2}{L}\sin^2\left(\frac{2\pi}{L}\cdot\frac{L}{2}\right) \times 0.2L = \boxed{0}$$

For the second excited state, $n = 3$. Therefore,

$$P_3 dx = \frac{2}{L}\sin^2\left(\frac{3\pi}{L}\cdot\frac{L}{2}\right) \times 0.2L = \boxed{0.4}$$

7.2 THREE-DIMENSIONAL INFINITE SQUARE WELL

The discussions of section 7.1 and problem 7.3 can be easily generalized to the case of a particle in a **three-dimensional box**. This problem is more closely related to actual physical systems.

Let us consider a particle of mass m constrained to move in a rectangular box shown in Figure 7.5. The origin O is at one corner of the box and the lengths of the box along x –, y – and z – axes are a, b and c, respectively. Inside the box the potential energy is zero and outside it is infinite.

The time-independent Schrödinger equation inside the box is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x, y, z) = E\psi(x, y, z)$$

or $$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad (7.23)$$

which is to be solved subject to the condition that $\psi(x, y, z) = 0$ at the walls of the box.

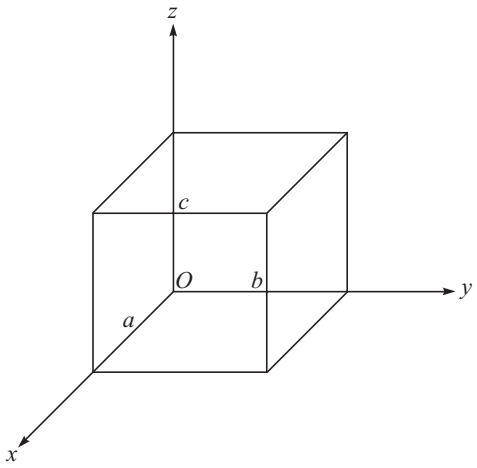

Figure 7.5 Three-dimensional box.

This partial differential equation can be solved by the technique of separation of variables. We assume that the function $\psi(x, y, z)$ can be written as a product of three functions each of which depends on only one of the coordinates:

$$\psi(x, y, z) = X(x)\ Y(y)\ Z(z) \tag{7.24}$$

Substituting into Equation (7.23) and dividing by XYZ, we get

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} + \frac{2mE}{\hbar^2} = 0 \tag{7.25}$$

Note that each term of this equation is a function of only one of the independent variables x, y, z and the last term is a constant. Therefore, this equation can be valid only if each term is a constant. We write

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2 \tag{7.26}$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -k_y^2 \tag{7.27}$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = -k_z^2 \tag{7.28}$$

where k_x, k_y, k_z are constants. Equation (7.25) reduces to

$$k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} \tag{7.29}$$

Each of the three Equations (7.26), (7.27) and (7.28) depends on only one of the variables and, therefore, can be solved easily. Equation (7.26) can be rewritten as

$$\frac{d^2X}{dx^2} + k_x^2 X = 0 \tag{7.30}$$

The general solution of this equation is

$$X(x) = A \sin k_x x + B \cos k_x x$$

The boundary condition $X(0) = 0$ makes $B = 0$. The boundary condition $X(a) = 0$ gives

$$k_x a = n_x \pi$$

or
$$k_x = \frac{n_x \pi}{a}, \qquad n_x = 1, 2, 3\ldots \tag{7.31}$$

Thus the normalized solution to (7.30) is

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}, \qquad n_x = 1, 2, 3\ldots \tag{7.32}$$

Similarly, for $Y(y)$ and $Z(z)$ we have,

$$k_y = \frac{n_y \pi}{b}, \qquad n_y = 1, 2, 3,\ldots \tag{7.33}$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}, \qquad n_y = 1, 2, 3,\ldots \tag{7.34}$$

$$k_z = \frac{n_z \pi}{c}, \qquad n_z = 1, 2, 3,\ldots \tag{7.35}$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}, \quad n_z = 1, 2, 3,\ldots \tag{7.36}$$

Combining (7.32), (7.34) and (7.36), we obtain the **normalized eigenfunctions:**

$$\boxed{\psi_{n_x,n_y,n_z}(x, y, z) = \left(\frac{8}{abc}\right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}} \tag{7.37}$$

where n_x, n_y, n_z = 1,2,3...

Now, substituting (7.31), (7.33) and (7.35) into (7.29) and rearranging, we get the expression for the **energy** E as

$$\boxed{E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \tag{7.38}$$

Note that there are three quantum numbers that are necessary to describe each quantum state. This is a general property of all three-dimensional systems. For the ground state $n_x = n_y = n_z = 1$. However, the set of quantum numbers which defines the first and the higher states depends on the relative magnitudes of a, b, and c.

Let us consider the simplest case of a **cubical box**. Then $a = b = c$ and the **energy eigenvalues** become

$$\boxed{E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)} \tag{7.39}$$

The corresponding **eigenfunctions** are

$$\boxed{\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{8}{a^3}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)} \quad (7.40)$$

Taking $n_x = n_y = n_z = 1$, the ground state energy is

$$E_{1,1,1} = \frac{3\pi^2\hbar^2}{2ma^2} \quad (7.41)$$

This state is *nondegenerate*. The next higher energy, which is twice of this, can be obtained in three different ways:

n_x	n_y	n_z
2	1	1
1	2	1
1	1	2

This shows that the first excited state is *three-fold degenerate*. It can be easily seen that most of the higher states are degenerate. The degeneracy occurs because the energy depends on the quantum numbers n_x, n_y and n_z only through the combination $n^2 = n_x^2 + n_y^2 + n_z^2$, and the same value of n can be obtained for different sets of values of n_x, n_y and n_z. Note that this is not true for the energy levels (7.38) of a rectangular box. The existence of degeneracies is thus related to the *symmetry* of the potential. This is one important way in which a multi-dimensional system differs from a one-dimensional system.

PROBLEM 7.9 Think of the nucleus as a cubical box of length 10^{-14} m. Compute the minimum energy of a nucleon confined to the nucleus. Given: mass of a nucleon = 1.6×10^{-27} kg.

Solution: From Equation (7.41) the ground state energy of a particle of mass m in a cubical box of length a is given by

$$E = \frac{3\pi^2\hbar^2}{2ma^2}$$

Therefore, the minimum energy of the nucleon is

$$E_{\min} = \frac{3 \times (3.14)^2 \times (1.054 \times 10^{-34})^2}{2 \times 1.6 \times 10^{-27} \times (10^{-14})^2}$$
$$= 9.75 \times 10^{-13} \text{ J}$$
$$= \boxed{6.1 \text{ MeV}}$$

7.3 ONE-DIMENSIONAL FINITE SQUARE WELL (FIRST TYPE)

The finite square well can be of two types. The first type is as shown in Figure 7.6 and will be discussed in this section. The second type is shown in Figure 7.8 and will be discussed in the next section.

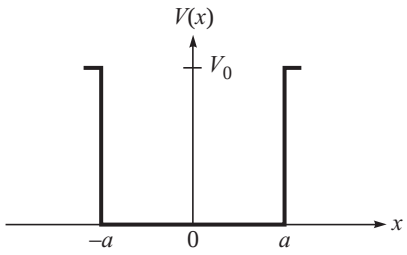

Figure 7.6 Finite square well (first type).

The square well potential shown in Figure 7.6 is given by

$$V(x) = \begin{cases} 0 & |x| < a \\ V_0 & |x| > a \end{cases} \tag{7.42}$$

Consider a particle of mass m moving in this potential with energy E. We shall consider the case when $\boldsymbol{E < V_0}$. The particle is then confined in a *bound state*. In the other case, when $E > V_0$ the particle is unconfined. This situation is relevant in the scattering of a particle by a potential. Such problems will be discussed in the next chapter.

Inside the well the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \qquad |x| < a$$

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \qquad k^2 = \frac{2mE}{\hbar^2} \tag{7.43}$$

The general solution of this equation is

$$\psi(x) = A \sin kx + B \cos kx \tag{7.44}$$

Outside the well the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi = E\psi, \qquad |x| > a$$

or

$$\frac{d^2\psi}{dx^2} - K^2\psi = 0, \quad K^2 = \frac{2m(V_0 - E)}{\hbar^2} \tag{7.45}$$

Since $V_0 > E$, the quantity K^2 is positive. Therefore, the general solution of this equation is

$$\psi(x) = Ce^{-Kx} + De^{Kx} \tag{7.46}$$

Now, the wave function should not become infinite as $x \to \pm\infty$. Therefore, we must take $C = 0$ for $x < -a$ and $D = 0$ for $x > a$. So, the wave function can be written as

$$\psi(x) = \begin{cases} De^{Kx} & x < -a \\ A\sin kx + B\cos kx & -a < x < a \\ Ce^{-Kx} & x > a \end{cases} \tag{7.47}$$

The requirement that $\psi(x)$ and $d\psi/dx$ be continuous at $x = -a$ gives

$$-A \sin ka + B \cos ka = De^{-Ka} \tag{7.48}$$

and

$$kA \cos ka + kB \sin ka = KDe^{-Ka} \tag{7.49}$$

Similarly, the continuity of $\psi(x)$ and $d\psi/dx$ at $x = a$ gives

$$A \sin ka + B \cos ka = Ce^{-Ka} \tag{7.50}$$

and

$$kA \cos ka - kB \sin ka = -KCe^{-Ka} \tag{7.51}$$

Equations (7.48) and (7.50) give

$$2A \sin ka = (C - D)\, e^{-Ka} \tag{7.52}$$

$$2B \cos ka = (C + D)\, e^{-Ka} \tag{7.53}$$

Equations (7.49) and (7.51) give

$$2kA \cos ka = -K\,(C - D)\, e^{-Ka} \tag{7.54}$$

$$2kB \sin ka = K\,(C + D)\, e^{-Ka} \tag{7.55}$$

Equations (7.52) and (7.54) yield

$$k \cot ka = -K \tag{7.56}$$

unless $A = 0$ and $C = D$. Similarly, Equations (7.53) and (7.55) yield

$$k \tan ka = K \tag{7.57}$$

unless $B = 0$ and $C = -D$.

Eliminating K from (7.56) and (7.57) leads to $\tan^2 ka = -1$ which is not possible because both k and a are real. Therefore, these two equations cannot be valid simultaneously. Thus, we have two classes of solutions:

For the *first class*

$$A = 0,\ C = D \qquad \text{and} \qquad k \tan ka = K \tag{7.58}$$

and for the *second class*

$$B = 0,\ C = -D \qquad \text{and} \qquad k \cot ka = -K \tag{7.59}$$

Eigenfunctions

The *eigenfunctions* of the *first class* are given by

$$\psi(x) = \begin{cases} Ce^{Kx} & x < -a \\ B\cos kx & -a < x < a \\ Ce^{-Kx} & x > a \end{cases} \tag{7.60}$$

The *eigenfunctions* of the *second class* are given by

$$\psi(x) = \begin{cases} Ce^{Kx} & x < -a \\ A\sin kx & -a < x < a \\ -Ce^{-Kx} & x > a \end{cases} \tag{7.61}$$

It is interesting to note that the eigenfunctions extend into the classically forbidden region $|x| > a$. The distance through which they extend is roughly $K^{-1} = \hbar/[2m(V_0 - E)]^{1/2}$, which increases as the energy E of the particle increases.

Parity

It may be noted, as in the case of the infinite square well, that the eigenfunctions of the first class have *even* parity, satisfying

$$\psi(-x) = \psi(x)$$

and the eigenfunctions of the second class have *odd* parity, satisfying

$$\psi(-x) = -\psi(x)$$

This division of eigenfunctions into even and odd types is due to the fact that the potential energy is symmetric about the origin, that is, $V(-x) = V(x)$.

Energy Levels

The energy levels can be found by solving the Equations (7.56) and (7.57) numerically or graphically. We shall describe a simple graphical procedure. Let us put $\xi = ka$ and $\eta = Ka$, so that Equations (7.57) and (7.56) become, respectively

$$\xi \tan \xi = \eta \tag{7.62}$$

$$\xi \cot \xi = -\eta \tag{7.63}$$

These equations are to be solved along with

$$\xi^2 + \eta^2 = (k^2 + K^2)a^2 = \frac{2mV_0a^2}{\hbar^2} = \gamma^2 \tag{7.64}$$

where $\gamma = (2mV_0 a^2/\hbar^2)^{1/2}$. Since ξ and η are positive, the energy levels may be obtained by determining the points of intersection in the first quadrant of the circle (7.64) with the curve (7.62) for even states or with the curve (7.63) for odd states. This is illustrated in Figure 7.7 for three values of γ (= 1, 2 and $\sqrt{12}$). For a given mass m of the particle, γ depends on the parameters of the square well through the combination V_0a^2. Thus it is a measure of the strength of the potential. It is found that for $\gamma = 1$, there is one even bound state and no odd bound state. For $\gamma = 2$, there is one even state and one odd state. For $\gamma = \sqrt{12}$, there are two even states and one odd state. Thus the three increasing values of γ give a total of one, two, and three energy levels, respectively.

The following conclusions are easily drawn:

(i) The energy levels are *nondegenerate*. This is expected because the potential is one-dimensional.

(ii) The number of energy levels is *finite* and depends on the strength parameter γ and hence on V_0a^2. If $(N-1)\,\pi/2 < \gamma \le N\pi/2$, then the total number of states is equal to N.

(iii) As γ increases, energy levels corresponding respectively to even and odd parity appear successively. The ground state is even, the next state is odd and so on.

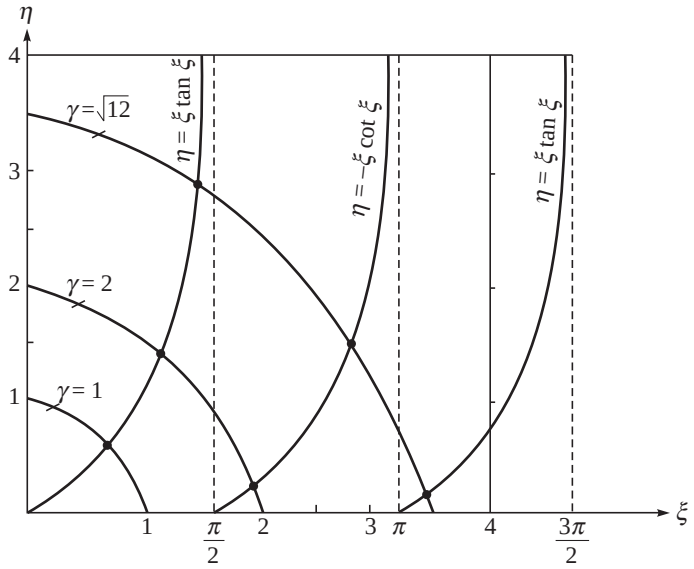

Figure 7.7 Graphical determination of the energy levels for a square well potential.

In the **limiting case** of infinite square well, $V_0 \to \infty$. In that case $\eta \to \infty$. The roots of Equations (7.62) and (7.63) will then be

$$\xi = \frac{n\pi}{2}, \qquad n = 1, 2, \ldots$$

Since $\xi = ka = (2mE/\hbar^2)^{1/2}\, a$, we get

$$\frac{2mEa^2}{\hbar^2} = \frac{n^2\pi^2}{4}$$

or

$$E = \frac{n^2\pi^2\hbar^2}{8ma^2}$$

which is same as the earlier result (7.13). Further, $K \to \infty$ when $V_0 \to \infty$. Therefore, the eigenfunctions (7.60) and (7.61) will vanish for $|x| > a$ as is the case for the infinte square well (section 7.1).

7.4 ONE-DIMENSIONAL FINITE SQUARE WELL (SECOND TYPE)

The finite square well of the second type is shown in Figure. 7.8. The potential is given by

$$V(x) = \begin{cases} -V_0 & |x| < a \\ 0 & |x| > a \end{cases} \tag{7.65}$$

It should be noted that the potentials in Figures 7.6 and 7.8 differ only in the origin of the energy scale and are, therefore, physically equivalent.

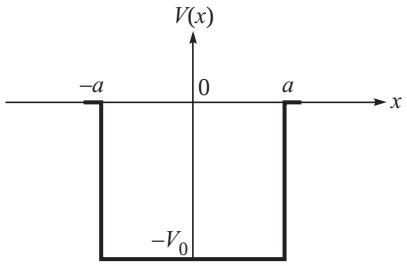

Figure 7.8 Finite square well (second type).

We shall discuss the case $\boldsymbol{E < 0}$ which gives rise to bound states. Inside the well the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi = -|E|\psi, \quad |x| < a$$

or
$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0, \quad \alpha^2 = \frac{2m(V_0 - |E|)}{\hbar^2} \tag{7.66}$$

Here $|E| = -E$ is the binding energy of the particle in the well. Since $V_0 > |E|$, the quantity α^2 is positive. Therefore, the general solution of this equation is

$$\psi(x) = A \sin \alpha x + B \cos \alpha x \tag{7.67}$$

Outside the well the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi = -|E|\psi, \quad |x| > a$$

or
$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0, \quad \beta^2 = \frac{2m|E|}{\hbar^2} \tag{7.68}$$

The general solution of this equation is

$$\psi(x) = Ce^{-\beta x} + De^{\beta x} \tag{7.69}$$

Now, the wave function should not become infinite as $x \to \pm\infty$. Therefore, we must take $C = 0$ for $x < -a$ and $D = 0$ for $x > a$. So the wave function can be written as

$$\psi(x) = \begin{cases} De^{\beta x} & x < -a \\ A\sin\alpha x + B\cos\alpha x & -a < x < a \\ Ce^{-\beta x} & x > a \end{cases} \tag{7.70}$$

Imposing the requirements that $\psi(x)$ and $d\psi/dx$ be continuous at $x = \pm a$ and carrying out the same manipulations as in the previous section, we obtain two classes of solutions.

The **eigenfunctions** of the *first class* are given by

$$\psi(x) = \begin{cases} Ce^{\beta x} & x < -a \\ B\cos\alpha x & -a < x < a \\ Ce^{-\beta x} & x > a \end{cases} \tag{7.71}$$

The **eigenfunctions** of the *second class* are given by

$$\psi(x) = \begin{cases} Ce^{\beta x} & x < -a \\ A\sin\alpha x & -a < x < a \\ -Ce^{-\beta x} & x > a \end{cases} \tag{7.72}$$

The **energy levels** can be found by solving the equations

$$\xi \tan \xi = \eta$$
$$\xi \cot \xi = -\eta$$

where $\xi = \alpha a$ and $\eta = \beta a$. These equations can be solved to obtain the energy levels following the same procedure as in the previous section.

SUMMARY

1. In this chapter we solve the time-independent Schrödinger equation for a particle constrained to move in a limited region. It is found that this confinement leads to quantization of energy. Three simple systems are discussed—the infinite square well in one and three dimensions and the finite square well in one dimension.

2. For a one-dimensional infinite square well, the potential energy is

$$V(x) = \begin{cases} 0 & |x| < a \\ \infty & |x| > a \end{cases}$$

The normalized eigenfunctions are found to be

$$\psi_n(x) = \begin{cases} \dfrac{1}{\sqrt{a}}\cos\dfrac{n\pi x}{2a}, & n = 1,3,5,\ldots \\ \dfrac{1}{\sqrt{a}}\sin\dfrac{n\pi x}{2a}, & n = 2,4,6,\ldots \end{cases}$$

Thus, the eigenfunctions are grouped into two classes—the first class consists of functions which have even parity and the second class consists of functions having odd parity. This division is a consequence of the symmetry of the potential: $V(-x) = V(x)$.

The energy eigenvalues are

$$E_n = \frac{n^2\pi^2\hbar^2}{8ma^2}, \qquad n = 1, 2, 3,\ldots$$

The energy levels are nondegenerate. The lowest possible energy is not zero, in agreement with the uncertainty principle.

3. For a three-dimensional box having the origin at one corner and having lengths a, b and c along the x-, y- and z-axis, respectively, the normalized eigenfunctions are

$$\psi_{n_x,n_y,n_z}(x, y, z) = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x\pi x}{a} \sin\frac{n_y\pi y}{b} \sin\frac{n_z\pi z}{c}$$

$$n_x, n_y, n_z = 1, 2, 3,\ldots$$

The energy eigenvalues are

$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

The energy levels are, in general, nondegenerate. However, if $a = b = c$, that is for a cubical box, the energy eigenvalues are given by

$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)$$

In this case most of the energy levels are degenerate. The ground state ($n_x = n_y = n_z = 1$) is, however, nondegenerate. The degeneracies are a consequence of the symmetry of the cubical potential.

4. For a one-dimensional finite square well, the potential energy is

$$V(x) = \begin{cases} 0 & |x| < a \\ V_0 & |x| > a \end{cases}$$

for a bound system the energy $E < V_0$. There are two classes of eigenfunctions. For the first class

$$\psi(x) = \begin{cases} Ce^{Kx} & x < -a \\ B\cos kx & -a < x < a \\ Ce^{-Kx} & x > a \end{cases}$$

where $k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$, $K = \left(\frac{2m(V_0 - E)}{\hbar^2}\right)^{1/2}$

For the second class

$$\psi(x) = \begin{cases} Ce^{Kx} & x < -a \\ A\sin kx & -a < x < a \\ -Ce^{-Kx} & x > a \end{cases}$$

The eigenfunctions extend into the classically forbidden region.

The energy levels can be found by graphical methods as discussed in the text. The energy levels are nondegenerate and the number of levels is finite.

QUESTIONS

1. Obtain the energy eigenvalues and the normalized eigenfunctions for a particle in a one-dimensional infinite square well. Draw the eigenfunctions and their absolute squares for the lowest four states.

2. Justify that the existence of a non-zero ground state energy for an infinite square well potential is in accordance with the uncertainty principle.

3. Consider a particle moving in an infinite potential well defined by

$$V(x, y, z) = \begin{cases} 0 & \text{for } 0 < x < a,\ 0 < y < b,\ 0 < z < c \\ \infty & \text{everywhere else} \end{cases}$$

Solve the time-independent Schrödinger equation for this system and obtain the energy eigenvalues and normalized eigenfunctions.

4. Consider a particle moving in a three-dimesional infinite square well defined by

$$V(x, y, z) = \begin{cases} 0 & \text{for } 0 < x < a,\ 0 < y < a,\ 0 < z < a \\ \infty & \text{everywhere else} \end{cases}$$

Solve the time-independent Schrödinger equation for this system and obtain the energy eigenvalues and the normalized eigenfunctions. Show that the ground state is nondegenerate whereas the first excited state is three-fold degenerate.

5. Consider a particle moving in a one-dimensional finite square well defined by

$$V(x) = \begin{cases} 0 & |x| < a \\ V_0 & |x| > a \end{cases}$$

Solve the time-independent Schrödinger equation for $E < V_0$, where E is the energy of the particle. Obtain the energy eigenfunctions and classify them according to parity. Discuss how the energy levels can be obtained graphically.

6. Consider a particle moving in a one-dimensional finite square well defined by

$$V(x) = \begin{cases} -V_0 & |x| < a \\ 0 & |x| > a \end{cases}$$

Solve the time-independent Schrödinger equation for the system and obtain the bound state energy eigenfunctions. Discuss how the energy levels can be obtained graphically.

EXERCISES

1. Consider an electron in an infinite well of width 0.5 Å. Calculate the energy of the electron in the (a) ground state, (b) first excited state. Mass of electron = 9.0×10^{-31}kg.

[***Ans.*** (a) 1.5×10^2 eV, (b) 6.0×10^2 eV]

2. An electron is trapped in an infinite well of width 1 cm. For what value of n will the electron have an energy of 1 eV? [***Ans.*** 1.5×10^7]

3. The lowest energy possible for a particle entrapped in a box is 40 eV. What are the next three higher energies the particle can have?

[***Ans.*** 160 eV, 360 eV, 640 eV]

4. Calculate the first three energy levels of an electron enclosed in a box of width 10 Å. Compare these energies with those of a glass marble of mass 1 g contained in a box of width 20 cm. Can these energies of the marble be measured experimentally?

[***Ans.*** For *electron*: 0.377 eV, 1.508 eV, 3.393 eV; for *marble*: 0.858×10^{-44} eV, 3.432×10^{-44} eV, 7.722×10^{-44} eV. These energies of the marble cannot be measured experimentally as these are very-very small (almost zero).]

5. An electron is trapped in a one-dimensional infinite potential well of width 1.0 Å. Calculate the wavelength of the photon emitted when the electron makes a transition from the first excited state to the ground state. In which region of the electromagnetic spectrum does this wavelength lie? [***Ans.*** 1.1×10^{-8} m, ultraviolet]

6. An electron of energy 342 eV is confined in a one-dimensional box of length 1.0 Å. Calculate (a) the quantum number n of the energy level of the electron and (b) the energy required to take the electron to the next higher level. [***Ans.*** (a) $n = 3$, (b) 266 eV]

7. A particle is moving in a one-dimensional box of width 10 Å. Calculate the probability of finding the particle within an interval of 2 Å at the centre of the box when it is in the state of least energy. [***Ans.*** 0.4]

8. An electron is confined in a cubical box of each side 1 Å. Calculate the energies of the electron in the ground state and the first excited state.

[***Ans.*** 113 eV, 226 eV]

9. Show that the de Broglie wavelength of a particle in a one-dimensional box in the first excited state is equal to the length of the box.

Chapter

8

Scattering of Particles by Barriers and Wells

Chapter Contents

8.1 The Potential Step
8.2 The Square Potential Barrier
8.3 Explanation of Alpha Decay
8.4 The Square Potential Well

In this chapter we shall discuss what happens when a beam of particles of fixed energy is incident on a potential barrier or well. Three simple systems are considered—the potential step, the square barrier and the square well. We shall see that in each case a certain fraction of the incident particles is transmitted, while the remaining fraction is reflected. This is in contrast to what is expected on the basis of classical mechanics. Classically, there must be total transmission if the energy of the incident particle is more than the height of the barrier, and total reflection if the energy of the incident particle is less than the height of the barrier.

The transmission of particles even when the particle energy is less than the barrier height is a unique quantum phenomenon and is known as *tunneling*. The tunnel effect has important consequences and applications, for example, radioactive alpha decay, tunnel diode, scanning tunneling microscope etc. We shall discuss the mechanism of alpha decay in detail.

8.1 THE POTENTIAL STEP

Let us consider the potential step shown in Figure 8.1. It is an infinite-width potential barrier given by

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases} \tag{8.1}$$

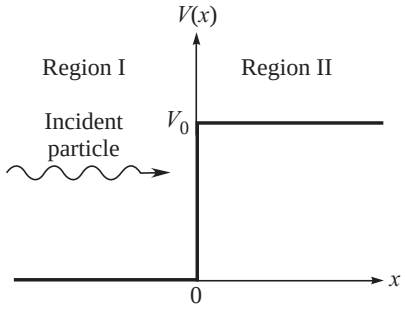

Figure 8.1 The potential step.

Suppose, a particle of mass m is incident on the step from the left with energy E. According to classical mechanics, if $E < V_0$, then the particle would be reflected back at $x = 0$ because it does not have sufficient energy to climb the barrier. On the other hand, if $E > V_0$, then the particle would not be reflected; it would keep moving towards the right with reduced energy.

We shall now study this system using quantum mechanics. Since the potential does not depend on time, the motion of the particle is described by the wave function $\Psi(x, t) = \psi(x) \exp(-iEt/\hbar)$, where $\psi(x)$ satisfies the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{8.2}$$

We shall discuss the solution of this equation separately for the two cases, $E > V_0$ and $E < V_0$.

Case 1: $E > V_0$

In **region I ($x < 0$)** the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

or
$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0, \qquad k^2 = \frac{2mE}{\hbar^2} \tag{8.3}$$

The general solution of this equation is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

where A and B are arbitrary constants. We know that physically the functions $\exp(ikx)$ and $\exp(-ikx)$, multiplied by the time-dependent function $\exp(-iEt/h)$, represent plane waves moving towards the right and towards the left, respectively. Therefore, the first term $A\exp(ikx)$ of $\psi(x)$ in region I corresponds to a plane wave of amplitude A incident on the potential step from the left and the second term $B\exp(-ikx)$ corresponds to a plane wave of amplitude B reflected from the step. Thus, according to quantum mechanics,

the particle may be reflected back at $x = 0$ even though $E > V_0$. This is not possible classically.

In **region II** $(x > 0)$ the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi = E\psi$$

or
$$\frac{d^2\psi}{dx^2} + k'^2\psi(x) = 0, \qquad k'^2 = \frac{2m(E-V_0)}{\hbar^2} \tag{8.4}$$

Since $E > V_0$, the quantity k'^2 is positive. Therefore, the general solution of this equation is

$$\psi(x) = Ce^{ik'x} + D\,e^{-ik'x}$$

Since we are considering a particle incident on the barrier from the left, we must discard the term $D \exp(-ik'x)$ which corresponds to a reflected wave in region II and there is nothing in this region which can cause such a reflection. Therefore, we must put $D = 0$. Thus the complete eigenfunction is given by

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik'x} & x > 0 \end{cases} \tag{8.5}$$

The eigenfunction consists of an *incident* wave of amplitude A and a *reflected* wave of amplitude B in region I, and a *transmitted* wave of amplitude C in region II. The wave number in region I is k and that in region II is k'.

Continuity of ψ and $d\psi/dx$ at $x = 0$ gives

$$A + B = C$$

and
$$k(A - B) = k'C$$

from which we obtain

$$\frac{B}{A} = \frac{k-k'}{k+k'} \tag{8.6}$$

and
$$\frac{C}{A} = \frac{2k}{k+k'} \tag{8.7}$$

Let us now obtain the probability current densities associated with the incident, the reflected and the transmitted waves. From Equation (6.33) we have

$$j = \mathrm{Re}\left[\psi^* \frac{\hbar}{im}\frac{\partial\psi}{\partial x}\right]$$

If j_{in}, j_{re} and j_{tr} represent the magnitudes of the probability current densities associated with the incident, the reflected and the transmitted waves, respectively, then we readily obtain

$$j_{in} = \frac{\hbar k}{m}|A|^2 \tag{8.8}$$

$$j_{re} = \frac{\hbar k}{m}|B|^2 \tag{8.9}$$

and

$$j_{tr} = \frac{\hbar k'}{m}|C|^2 \tag{8.10}$$

A particle incident on the step will either be reflected or transmitted. The probability of reflection is given by the **reflection coefficient** R:

$$\boxed{R = \frac{j_{re}}{j_{in}} = \left|\frac{B}{A}\right|^2 = \left(\frac{k-k'}{k+k'}\right)^2} \tag{8.11}$$

Substituting the values of k and k' and simplifying this becomes

$$\boxed{R = \left[\frac{1-(1-V_0/E)^{1/2}}{1+(1-V_0/E)^{1/2}}\right]^2, \quad E > V_0} \tag{8.12}$$

The probability of transmission is given by the **transmission coefficient** T:

$$\boxed{T = \frac{j_{tr}}{j_{in}} = \frac{k'}{k}\left|\frac{C}{A}\right|^2 = \frac{4kk'}{(k+k')^2}} \tag{8.13}$$

Substituting the values of k and k',

$$\boxed{T = \frac{4(1-V_0/E)^{1/2}}{[1+(1-V_0/E)^{1/2}]^2}, \quad E > V_0} \tag{8.14}$$

Note that R and T depend only on the ratio V_0/E. Note also that $R + T = 1$, as it must be, because the probability is conserved.

It can be easily shown that

$$k(|A|^2 - |B|^2) = k'|C|^2 \tag{8.15}$$

This shows that the net current incident on the step from the left is equal to the transmitted current.

Case 2: $E < V_0$

In region I the Schrödinger equation, its solution and interpretation remain the same as in case 1 ($E > V_0$). In region II the equation becomes

$$\frac{d^2\psi(x)}{dx^2} - K^2\psi(x) = 0, \quad K^2 = \frac{2m(V_0-E)}{\hbar^2} \tag{8.16}$$

Since $V_0 > E$, the quantity K^2 is positive. Therefore, the general solution of this equation is

$$\psi(x) = Ce^{-Kx} + De^{Kx}$$

Now, the wave function should not become infinite at $x \to \infty$. Since $\exp(Kx)$ diverges in that limit, we must choose $D = 0$. Thus the complete eigenfunction is given by

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{-Kx} & x > 0 \end{cases} \tag{8.17}$$

We note that the wave function is not zero in the classically forbidden region II, although it decreases rapidly as x increases. Thus there is a finite, though small, probability of finding the particle in region II. This phenomenon is called **barrier penetration** and is observed experimentally in various atomic and nuclear systems. It illustrates a fundamental difference between classical and quantum physics.

Note that $k' = iK$. Therefore the reflection coefficient can be immediately written as (using (8.11)):

$$R = \left| \frac{k - iK}{k + iK} \right|^2 = 1 \tag{8.18}$$

Since the eigenfunction is now real in region II, the transmitted probability current is zero according to Equation (6.33). Therefore, the transmission coefficient is zero:

$$T = 0 \tag{8.19}$$

These results show that although there is a finite probability of finding the particle in the classically-forbidden region II, there is no permanent penetration. It means that there is continuous reflection in region II until all the incident particles are ultimately returned to region I.

Figure 8.2 illustrates schematically the eigenfunctions for the step potential for the two cases, $E > V_0$ and $E < V_0$. Note that for $E > V_0$, the amplitude of the wave is larger in region II. The reason is that the velocity of the particle is

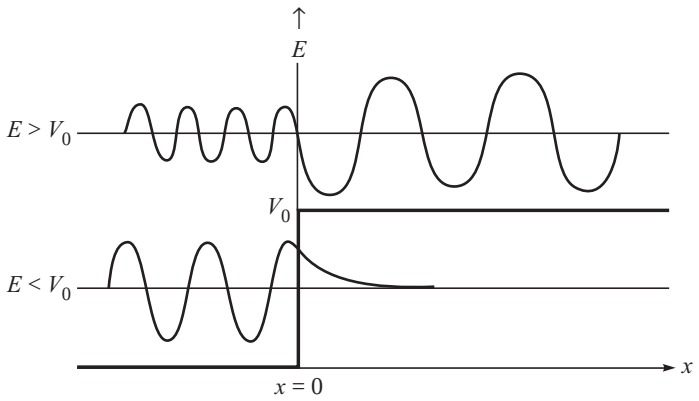

Figure 8.2 Eigenfunctions for the step potential.

smaller in this region and, therefore, it spends more time there. The wavelength is also larger in region II because the kinetic energy is lower in this region. For $E < V_0$, the eigenfunction is exponentially decaying but nonzero in region II.

Figure 8.3 shows the variation of reflection and transmission coefficients with E/V_0.

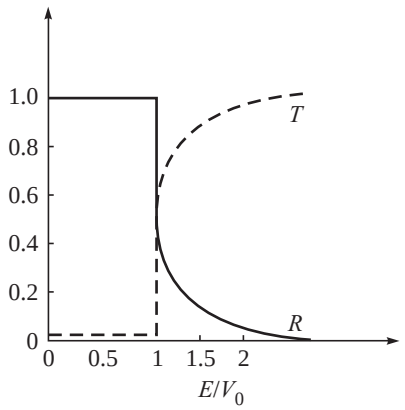

Figure 8.3 Variation of reflection and transmission coefficients with E/V_0.

PROBLEM 8.1 For a particle scattered by a potential step show that the sum of the reflection and transmission coefficients is one.

Solution: For $E > V_0$,

$$R + T = \frac{(k-k')^2}{(k+k')^2} + \frac{4kk'}{(k+k')^2} = \frac{(k+k')^2}{(k+k')^2} = 1$$

For $E < V_0$,

$$R + T = 1 + 0 = 1$$

PROBLEM 8.2 A particle of energy E is incident on a potential step of height V_0. What should be the ratio E/V_0 so that the probability of transmission is 50%?

Solution: Using (8.13),

$$T = \frac{4kk'}{(k+k')^2} = \frac{1}{2}$$

or $$k^2 + k'^2 = 6kk'$$

or $$\frac{2mE}{\hbar^2} + \frac{2m(E-V_0)}{\hbar^2} = \frac{6(\sqrt{2mE})(\sqrt{2m(E-V_0)})}{\hbar^2}$$

or $$E + E - V_0 = 6\sqrt{E(E-V_0)}$$

Squaring both sides,

$$4E^2 - 4EV_0 + V_0^2 = 36E^2 - 36EV_0$$

or $$32E^2 - 32EV_0 - V_0^2 = 0$$

or $$32\left(\frac{E}{V_0}\right)^2 - 32\left(\frac{E}{V_0}\right) - 1 = 0$$

Solving this we get

$$\frac{E}{V_0} = \frac{32 \pm \sqrt{32^2 + 128}}{64}$$

$$= \frac{1 \pm \sqrt{9/8}}{2} = \frac{1 \pm 1.06}{2}$$

$$= 1.03 \text{ or } -0.03$$

Since negative value is not possible,

$$\frac{E}{V_0} = \boxed{1.03}$$

PROBLEM 8.3 A particle of kinetic energy 9 eV is incident on a potential step of height 5 eV. Calculate the reflection coefficient.

Solution: $$R = \left(\frac{k - k'}{k + k'}\right)^2$$

$$k - k' = \frac{\sqrt{2m}}{\hbar}(\sqrt{E} - \sqrt{E - V_0})$$

$$k + k' = \frac{\sqrt{2m}}{\hbar}(\sqrt{E} + \sqrt{E - V_0})$$

So $$\frac{k - k'}{k + k'} = \frac{\sqrt{E} - \sqrt{E - V_0}}{\sqrt{E} + \sqrt{E - V_0}} = \frac{\sqrt{9} - \sqrt{9 - 5}}{\sqrt{9} + \sqrt{9 - 5}} = \frac{1}{5}$$

$\Rightarrow$ $$R = \left(\frac{1}{5}\right)^2 = \frac{1}{25} = \boxed{0.04}$$

PROBLEM 8.4 An electron of energy E is incident on a potential step of height $V_0 = 10$ eV. Calculate the reflection coefficient R and the transmission coefficient T when (a) $E = 5$ eV, (b) $E = 15$ eV, and (c) $E = 10$ eV.

Solution: (a) Here $E < V_0$. Therefore

$$R = \boxed{1}, \; T = \boxed{0}$$

(b) $$R = \left[\frac{\sqrt{E}-\sqrt{E-V_0}}{\sqrt{E}+\sqrt{E-V_0}}\right]^2 = \left[\frac{\sqrt{15}-\sqrt{15-10}}{\sqrt{15}+\sqrt{15-10}}\right]^2$$

$$= \left[\frac{\sqrt{15}-\sqrt{5}}{\sqrt{15}+\sqrt{5}}\right]^2$$

$$= \left(\frac{3.873-2.236}{3.873+2.236}\right)^2$$

$$= \left(\frac{1.637}{6.109}\right)^2 = \boxed{0.072}$$

$$T = 1 - R = 1 - 0.072 = \boxed{0.928}$$

(c) Here $E = V_0$. Therefore,

$$R = \boxed{1}, \quad T = \boxed{0}$$

8.2 THE SQUARE POTENTIAL BARRIER

We now consider a one-dimensional potential barrier of finite width and height given by

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 < x < a \\ 0 & x > a \end{cases} \tag{8.20}$$

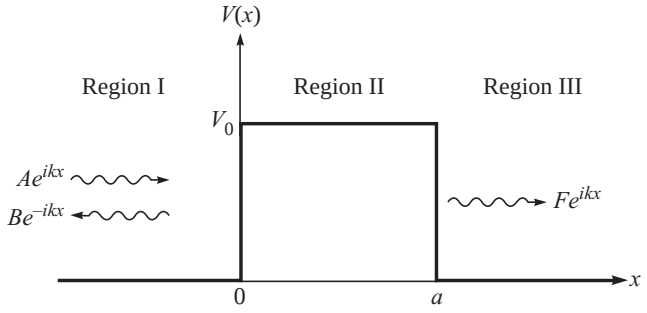

Figure 8.4 The square potential barrier.

Such a barrier is called a *square* or a *rectangular* barrier and is shown in Figure 8.4. Although the potential barriers in the real world do not have such simple shapes, this idealized treatment forms the basis for the understanding of more complicated systems and often provides a fairly good order-of-magnitude estimate.

As in the previous section, we consider a particle of mass m incident on the barrier from the left with energy E. As mentioned therein, according to classical

mechanics, the particle would always be reflected back if $E < V_0$ and would always be transmitted if $E > V_0$. We shall show that, quantum mechanically, both reflection and transmission occur with finite probability for all values of E except in some special cases.

We shall discuss the two cases, $E > V_0$ and $E < V_0$, separately.

Case 1: $E > V_0$

Let us divide the whole space into three regions: Region I ($x < 0$), Region II ($0 < x < a$) and Region III ($x > a$). In regions I and III the particle is free and so the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\ \psi(x)$$

or
$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0, \quad k^2 = \frac{2mE}{\hbar^2} \tag{8.21}$$

The general solution of this equation is

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Fe^{ikx} + Ge^{-ikx} & x > a \end{cases}$$

where A, B, F, G are arbitrary constants. For $x < 0$, the term $A\exp(ikx)$ corresponds to a plane wave of amplitude A incident on the barrier from the left and the term $B\exp(-ikx)$ corresponds to a plane wave of amplitude B reflected from the barrier. For $x > a$, the term $F\exp(ikx)$ corresponds to a transmitted wave of amplitude F. Since no reflected wave is possible in this region we must set $G = 0$.

In region II the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V_0\psi = E\psi$$

or
$$\frac{d^2\psi}{dx^2} + k'^2\psi(x) = 0, \quad k'^2 = \frac{2m(E - V_0)}{\hbar^2} \tag{8.22}$$

Since $E > V_0$, the quantity k'^2 is positive. Therefore, the general solution of this equation is

$$\psi(x) = Ce^{ik'x} + De^{-ik'x} \quad 0 < x < a$$

The complete eigenfunction is given by

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik'x} + De^{-ik'x} & 0 < x < a \\ Fe^{ikx} & x > a \end{cases} \tag{8.23}$$

The real part of the barrier eigenfunction for $E > V_0$ is shown schematically in Figure 8.5(a).

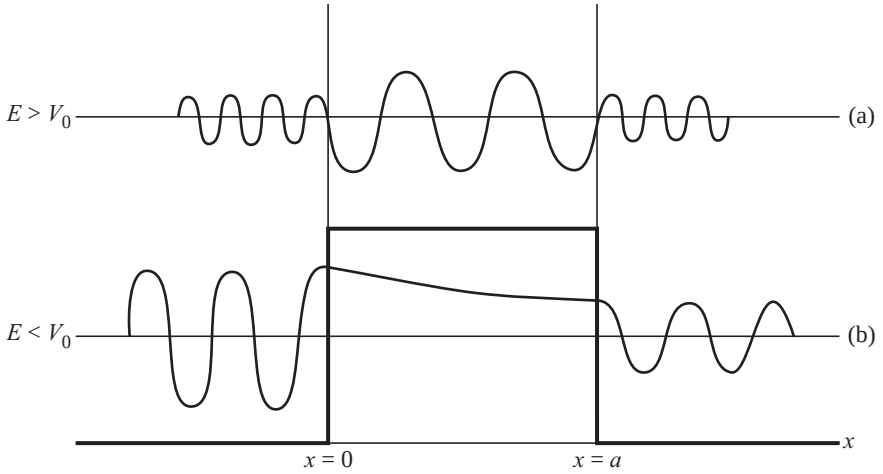

Figure 8.5 Schematic plots of the real parts of the barrier eigenfunctions for (a) $E > V_0$ and (b) $E < V_0$.

Continuity of $\psi(x)$ and $d\psi(x)/dx$ at $x = 0$ and $x = a$ gives

$$A + B = C + D \tag{8.24}$$

$$ik\,(A - B) = ik'\,(C - D) \tag{8.25}$$

$$Ce^{ik'a} + De^{-ik'a} = Fe^{ika} \tag{8.26}$$

$$ik'\,(Ce^{ik'a} - De^{-ik'a}) = ikFe^{ika} \tag{8.27}$$

From (8.24) and (8.25) we obtain

$$A = \frac{1}{2k}[C(k + k') + D(k - k')] \tag{8.28}$$

$$B = \frac{1}{2k}[C(k - k') + D(k + k')] \tag{8.29}$$

From (8.26) and (8.27) we obtain

$$C = \frac{1}{2k'}\,F(k' + k)\,e^{i(k - k')a} \tag{8.30}$$

$$D = \frac{1}{2k'}\,F(k' - k)\,e^{i(k + k')a} \tag{8.31}$$

Dividing (8.31) by (8.30)

$$\frac{D}{C} = \frac{k' - k}{k' + k}\,e^{2ik'a} \tag{8.32}$$

Dividing (8.29) by (8.28)

$$\frac{B}{A} = \frac{(k-k') + \left(\frac{D}{C}\right)(k+k')}{(k+k') + \left(\frac{D}{C}\right)(k-k')}$$

On substitution for D/C from (8.32), this becomes

$$\frac{B}{A} = \frac{(k^2 - k'^2)(1 - e^{2ik'a})}{(k+k')^2 - (k-k')^2 e^{2ik'a}} \tag{8.33}$$

We need a similar expression for F/A. Equations (8.24) and (8.25) yield

$$C = \frac{1}{2k'}[A(k + k') - B(k - k')]$$

Substituting in (8.30)

$$A(k + k') - B(k - k') = F(k + k')e^{i(k - k')a}$$

or

$$\frac{F}{A}(k + k')e^{i(k - k')a} = (k + k') - \frac{B}{A}(k - k')$$

$$= (k + k') - \left[\frac{(k^2 - k'^2)(1 - e^{2ik'a})}{(k+k')^2 - (k-k')^2 e^{2ik'a}}\right](k - k')$$

Simplifying, we obtain

$$\frac{F}{A} = \frac{4kk' e^{i(k'-k)a}}{(k+k')^2 - (k-k')^2 e^{2ik'a}} \tag{8.34}$$

The **reflection** and **transmission coefficients** are, respectively,

and

$$R = \left|\frac{B}{A}\right|^2 = \left[1 + \frac{4k^2k'^2}{(k^2 - k'^2)^2 \sin^2 k'a}\right]^{-1} = \left[1 + \frac{4E(E - V_0)}{V_0^2 \sin^2 k'a}\right]^{-1} \tag{8.35}$$

$$T = \left|\frac{F}{A}\right|^2 = \left[1 + \frac{(k^2 - k'^2)^2 \sin^2 k'a}{4k^2k'^2}\right]^{-1} = \left[1 + \frac{V_0^2 \sin^2 k'a}{4E(E - V_0)}\right]^{-1} \tag{8.36}$$

It can be easily shown that, as expected,

$$R + T = 1$$

Note that T is in general less than unity. This is in contradiction to the classical result that the particle always crosses the barrier when $E > V_0$. Here $T = 1$ only when $k'a = \pi, 2\pi, 3\pi, \ldots$. Now, if λ' is the de Broglie wavelength of the particle when it is passing through the barrier, then

$$k' = \frac{2\pi}{\lambda'}$$

Therefore $T = 1$ when

$$a = n\left(\frac{\lambda'}{2}\right), \quad n = 1, 2, 3, \ldots$$

Thus, there is *perfect transmission* only when the thickness of the barrier is equal to an integral multiple of half the de Broglie wavelength in the internal region. This is analogous to the interference phenomena in the transmission of light through thin refracting layers.

Equation (8.36) shows that

$$T \to \left[1 + \frac{mV_0 a^2}{2\hbar^2}\right]^{-1} \text{ as } E \to V_0 \text{ (from above)} \tag{8.37}$$

As E increases, T oscillates between a steadily increasing lower envelope and unity, as shown in Figure 8.6. The dimensionless parameter $mV_0a^2/\hbar^2$ is considered as a measure of the 'opacity' of the barrier.

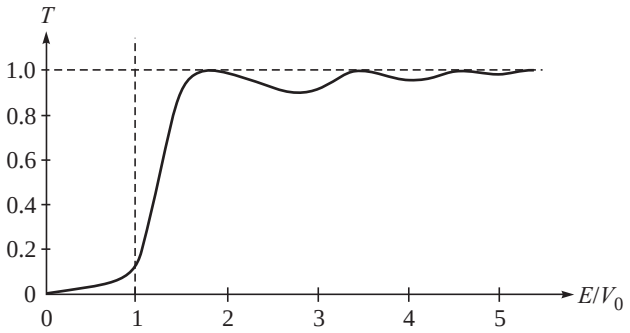

Figure 8.6 Variation of transmission coefficient for a square potential barrier as a function of E/V_0 for $mV_0a^2/\hbar^2 = 10$.

Case 2: $E < V_0$

In region I ($x < 0$) and III ($x > a$), the Schrödinger equation and its solution remain the same as in case 1. In region II ($0 < x < a$) the Schrödinger equation is

$$\frac{d^2\psi}{dx^2} - K^2\psi(x) = 0, \quad K^2 = \frac{2m(V_0 - E)}{\hbar^2} \tag{8.38}$$

Therefore, the eigenfunction in region II is

$$\psi(x) = Ce^{-Kx} + De^{Kx} \quad 0 < x < a \tag{8.39}$$

The real part of the complete eigenfunction for $E < V_0$ is shown schematically in Figure 8.5(b).

The **reflection** and **transmission coefficients** can be immediately obtained if we replace k' by iK in (8.35) and (8.36). Remembering that $\sin ix = i \sinh x$, we obtain

and

$$R = \left[1 + \frac{4k^2K^2}{(k^2+K^2)^2 \sinh^2(Ka)}\right]^{-1} = \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(Ka)}\right]^{-1} \tag{8.40}$$

$$T = \left[1 + \frac{(k^2+K^2)^2 \sinh^2(Ka)}{4k^2K^2}\right]^{-1} = \left[1 + \frac{V_0^2 \sinh^2(Ka)}{4E(V_0 - E)}\right]^{-1} \tag{8.41}$$

It is again readily verified that $R + T = 1$. We note that $T \to 0$ in the limit $E \to 0$. Further, T is a monotonically increasing function of E and approaches

$$\left[1 + \frac{mV_0a^2}{2\hbar^2}\right]^{-1} \quad \text{as } E \to V_0 \text{ (from below)} \tag{8.42}$$

Thus T joins smoothly to the value given in (8.37) for the case $E \to V_0$ from above (see Figure 8.6).

For a broad high barrier, $Ka >> 1$. This is true for most cases of practical interest. We may take $\sinh Ka \approx \exp(Ka)/2$. In that case,

$$T \approx \left(\frac{4kK}{k^2+K^2}\right)^2 e^{-2Ka} = \frac{16E(V_0 - E)}{V_0^2} e^{-2Ka} \tag{8.43}$$

and is very small.

Further, the factor $16E(V_0 - E)/V_0^2$ varies slowly with V_0 and E and is of order unity in most cases. The exponential factor is the dominant one and varies rapidly with V_0 and E. Therefore, for order of magnitude calculation, we can take

$$T \approx e^{-2Ka} \tag{8.44}$$

Variable Potential Barrier

In actual physical systems the potential barrier is not simple square type—the potential energy is variable (see for example, Figure 8.7). It is possible to have an estimate of the transmission coefficient in the case of such potentials by noticing that the quantity Ka is geometrically an area. If K varies with x, then this expression can be generalized to $\int_{x_1}^{x_2} K(x)\, dx$, where

$$K(x) = \frac{\sqrt{2m(V(x) - E)}}{\hbar}$$

We therefore have

$$T \approx \exp\left[-\frac{2}{\hbar}\int_{x_1}^{x_2} \sqrt{2m(V(x) - E)}\, dx\right] \tag{8.45}$$

x_1 and x_2 are the classical turning points, i.e., the points at which $V(x) = E$.

The most important and striking thing to note is that the particle has a nonzero probability of passing through a potential barrier which is completely

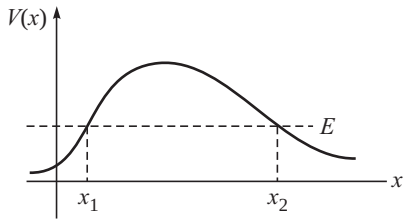

Figure 8.7 Variable potential barrier.

opaque classically. This phenomenon is known as **barrier penetration** or **tunnel effect** and illustrates a fundamental difference between classical and quantum mechanics. It is used in explaining various phenomena in atomic, nuclear and solid state physics. In the next section we discuss how tunnel effect can be used in explaining the emission of alpha particles by radioactive nuclei.

PROBLEM 8.5 Obtain Equation (8.43) from Equation (8.41).

Solution: If $Ka >> 1$, then $\sinh^2(Ka) >> 1$. Therefore, Equation (8.41) reduces to

$$T \approx \frac{4k^2K^2}{(k^2+K^2)^2 \sinh^2(Ka)} = \frac{4E(V_0-E)}{V_0^2 \sinh^2(Ka)}$$

Now,

$$\sinh(Ka) = \frac{e^{Ka}-e^{-Ka}}{2} = \frac{e^{-Ka}}{2}\left(e^{2Ka}-1\right) \approx \frac{\left(e^{-Ka}\right)\left(e^{2Ka}\right)}{2}$$

$$= \frac{e^{Ka}}{2}$$

Substituting in the above equation

$$T = \frac{4k^2K^2}{(k^2+K^2)^2}\left(\frac{2}{e^{Ka}}\right)^2 = \frac{4E(V_0-E)}{V_0^2}\left(\frac{2}{e^{Ka}}\right)^2$$

or
$$T = \left(\frac{4kK}{k^2+K^2}\right)^2 e^{-2Ka} = \frac{16E(V_0-E)}{V_0^2}e^{-2Ka}$$

PROBLEM 8.6 Electrons of energy 2.0 eV are incident on a barrier 3.0 eV high and 0.4 nm wide. Calculate the transmission probability.

Solution: Transmission probability $T = \left[1+\frac{V_0^2 \sinh^2(Ka)}{4E(V_0-E)}\right]^{-1}$

Here $V_0 - E = (3.0 - 2.0) = 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

$$Ka = \frac{[2m(V_0 - E)]^{1/2}}{\hbar}\, a$$

$$= \frac{[2 \times 9 \times 10^{-31} \times 1.6 \times 10^{-19}]^{1/2}}{1.05 \times 10^{-34}} \times 4 \times 10^{-10}$$

$$= 2.045$$

$$\sinh\,(2.045) = 3.805$$

$$\frac{V_0^2}{4E\,(V_0 - E)} = \frac{(3.0)^2}{4 \times 2.0 \times 1.0} = \frac{9}{8} = 1.125$$

$$T = [1 + 1.125 \times (3.805)^2]^{-1}$$

$$= \boxed{0.058}$$

PROBLEM 8.7 In problem 8.6, what would be the transmission probability if the width of the barrier changes to 0.1 nm?

Solution: In this case

$$Ka = 0.511$$

$$\sinh(0.511) = 0.5335$$

$$T = [1 + 1.125 \times (0.5335)]^{-1}$$

$$= \boxed{0.757}$$

Note that the transmission probability changes drastically from 5.8% to 75.7% when the width of the barrier is reduced to one-fourth of the original value. Thus, T is a very sensitive function of the barrier width a.

PROBLEM 8.8 An α-particle having energy 10 MeV approaches a square potential barrier of height 30 MeV. Determine the width of the barrier if the transmission coefficient is 2×10^{-3}. Given: mass of an α-particle = 6.68×10^{-27} kg, $\hbar = 1.054 \times 10^{-34}$ Js.

Solution: We shall use the approximate formula (8.43):

$$T = 16\left(\frac{E}{V_0}\right)\left(1 - \frac{E}{V_0}\right) e^{-2Ka}$$

where $$K = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

This, gives

$$e^{2Ka} = \frac{16}{T}\left(\frac{E}{V_0}\right)\left(1 - \frac{E}{V_0}\right)$$

or $$a = \frac{1}{2K}\left[2.303 \log_{10}\left\{\frac{16}{T}\left(\frac{E}{V_0}\right)\left(1 - \frac{E}{V_0}\right)\right\}\right]$$

Now,

$$K = \frac{\sqrt{2 \times 6.68 \times 10^{-27} \times (30 - 10) \times 10^{6} \times 1.6 \times 10^{-19}}}{1.054 \times 10^{-34}}$$

$$= 19.62 \times 10^{14}$$

Therefore $$a = \frac{10^{-14}}{2 \times 19.62}\left[2.303 \log_{10}\left\{\left(\frac{16}{2 \times 10^{-3}}\right)\left(\frac{1}{3}\right)\left(\frac{2}{3}\right)\right\}\right]$$

Simplifying we obtain

$$a = \boxed{1.91 \times 10^{-15} \text{ m}}$$

8.3 EXPLANATION OF ALPHA DECAY

The decay of a nucleus by alpha particle emission was first successfully explained in 1928 by Gamow and independently by Gurney and Condon on the basis of quantum tunneling. An alpha particle consists of two protons and two neutrons. The nature of the nuclear force is such that this combination has large binding energy and hence forms a stable structure. Therefore, it is reasonable to assume that alpha particles exist inside the nucleus, at least for a short time before emission. The forces acting on the alpha particle are the strongly attractive nuclear forces due to the other nucleons and the repulsive coulomb forces due to the other protons. Inside the nucleus the nuclear forces dominate but outside the nucleus these forces are negligible because of their short range. The potential energy of an alpha particle may, therefore, be represented schematically by the curve shown in Figure 8.8. Inside the nucleus ($r < R_0$), the

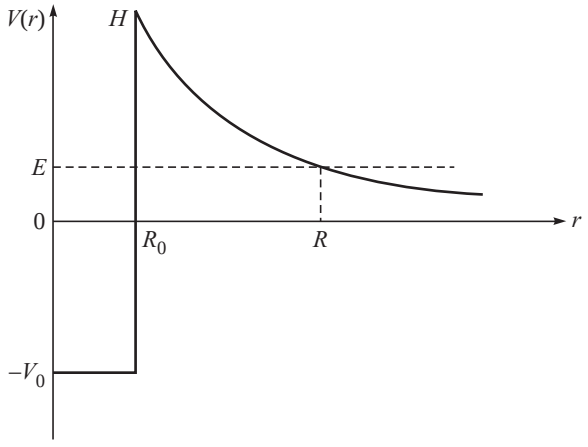

Figure 8.8 Potential energy of an alpha particle as a function of the distance r from the centre of a nucleus of radius R_0.

potential $V(r)$ can be taken to be a square well of depth V_0. Outside the nucleus, the potential is simply due to the Coulomb repulsion and is given by

$$V(r) = \frac{2Ze^2}{4\pi\varepsilon_0 r} \quad r > R_0 \tag{8.46}$$

Here Ze is the charge on the daughter nucleus and $2e$ is that on the alpha particle.

Figure 8.8 also shows the total energy E of the particle. This is also the kinetic energy with which the alpha particle emerges at a large distance from the nucleus because the Coulomb repulsion becomes vanishingly small at large r.

In turns out that the height H of the potential barrier is much larger than E. For example, in the case of ^{238}U, $H \approx 30$ MeV. On the other hand $E \approx 5 - 6$ MeV in most cases. Therefore the emission of alpha particles is not possible classically. In order to escape from the nucleus the alpha particle has to tunnel through the potential barrier in the region from R_0 to R, where R is the classical turning point given by

$$V(R) = E$$

or

$$\frac{2Ze^2}{4\pi\varepsilon_0 R} = E$$

or

$$R = \frac{2Ze^2}{4\pi\varepsilon_0 E} \tag{8.47}$$

It is found that generally $R >> R_0$. For example, in the α-decay of $^{204}_{84}$Po, $E = 5.4$ MeV. Using (8.47), we find $R = 43$ fm. On the other hand $R_0 = 6.5$ fm. Thus, the barrier is very thick and the ratio $R_0/R << 1$.

The transmission coefficient for tunneling through the barrier can be obtained using Equation (8.45). We write

$$T = e^{-G} \tag{8.48}$$

where

$$G = 2\left(\frac{2m}{\hbar^2}\right)^{1/2} \int_{R_0}^{R} \left[\frac{2Ze^2}{4\pi\varepsilon_0 r} - E\right]^{1/2} dr \tag{8.49}$$

Using (8.47) we can rewrite this as

$$G = 2\left(\frac{4m\,Ze^2}{4\pi\varepsilon_0\hbar^2}\right)^{1/2} \int_{R_0}^{R} \left(\frac{1}{r} - \frac{1}{R}\right)^{1/2} dr$$

Solving the integral we get

$$G = 2\left(\frac{4m\,Ze^2\,R}{4\pi\varepsilon_0\hbar^2}\right)^{1/2} \left[\cos^{-1}\left(\frac{R_0}{R}\right)^{1/2} - \left(\frac{R_0}{R} - \frac{R_0^2}{R^2}\right)^{1/2}\right] \tag{8.50}$$

We have seen above that $R_0/R << 1$. Using the fact that, for small x, $\cos^{-1} x \approx (\pi/2) - x$, (8.50) reduces to

$$G \approx 2\left(\frac{4m\,Ze^2\,R}{4\pi\varepsilon_0\,\hbar^2}\right)^{1/2}\left[\frac{\pi}{2} - 2\left(\frac{R_0}{R}\right)^{1/2}\right]$$

Substituting in (8.48) and using (8.47), we obtain

$$T \approx \exp\left[-\frac{2\pi\,Ze^2}{4\pi\varepsilon_0\,\hbar}\left(\frac{2m}{E}\right)^{1/2} + \frac{8}{\hbar}\left(\frac{Ze^2}{4\pi\varepsilon_0}\,MR\right)^{1/2}\right] \tag{8.51}$$

Inside the nucleus the alpha particle keeps bouncing back and forth and strikes the barrier wall periodically till emission occurs. The transmission coefficient gives the probability of emission in each encounter. It v is the average velocity of the alpha particle, then the number of encounters per unit time is $v/2R$. Therefore, the probability of emission per unit time, that is, the decay constant λ is

$$\lambda = \frac{v}{2R}\,T$$

We can take $v = (2E/m)^{1/2}$, which is same as the velocity of the alpha particle outside the nucleus.

The lifetime of the alpha particle in the nucleus is given by

$$\tau = \frac{1}{\lambda} = \left(\frac{2R}{v}\right)\frac{1}{T} = 2R\left(\frac{m}{2E}\right)^{1/2}\frac{1}{T}$$

Substituting the expression (8.51) for T and taking log of both sides, we obtain

$$\log\,\tau = \log\left[2R\left(\frac{m}{2E}\right)^{1/2}\right] + \frac{C}{\sqrt{E}} - D \tag{8.52}$$

where C and D are constants. Although the first term on the right also depends on E, this dependence is logarithmic and hence very weak. As such, τ depends on energy mainly according to the second term $C/\sqrt{E}$, which in turn depends on the tunneling through the barrier. Thus, to a fairly good approximation

$$\boxed{\log\,\tau = \frac{C_1}{\sqrt{E}} - C_2} \tag{8.53}$$

where C_1 and C_2 are constants. This formula gives a good fit to the experimental data of a large number of alpha emitters.

8.4 THE SQUARE POTENTIAL WELL

In section 7.4 we discussed the case of a particle of energy $E < 0$ confined in a square well of depth V_0. It was found that in this case the particle remains in a bound state and has discrete energy levels. Let us now discuss the scattering of a particle of energy $E > 0$ from a square potential well. We shall consider the well shown in Figure 8.9. It is given by

$$V(x) = \begin{cases} 0 & x < 0 \\ -V_0 & 0 < x < a \\ 0 & x > a \end{cases} \tag{8.54}$$

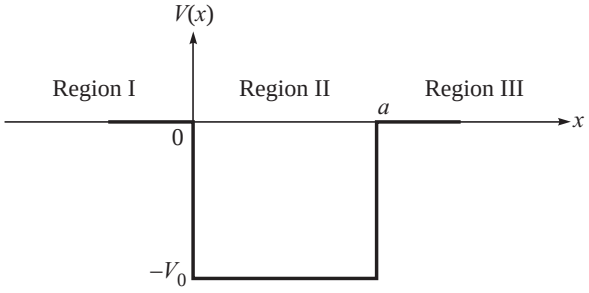

Figure 8.9 One-dimensional square well of depth V_0 and range a.

This potential has depth V_0 and range a. Suppose that the particle is incident upon the well from the left. Let us divide the whole space into three regions: Region I ($x < 0$), Region II ($0 < x < a$) and Region III ($x > a$). In the external regions I and III the particle is free and so the time independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi$$

or
$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0, \quad k^2 = \frac{2mE}{\hbar^2} \tag{8.55}$$

In the interior region II, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - V_0\psi = E\psi$$

or
$$\frac{d^2\psi(x)}{dx^2} + \beta^2\psi(x) = 0, \quad \beta^2 = \frac{2m(E+V_0)}{\hbar^2} \tag{8.56}$$

Solving Equations (8.55) and (8.56), we obtain the physically acceptable wave function

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{i\beta x} + De^{-i\beta x} & 0 < x < a \\ Fe^{ikx} & x > a \end{cases} \tag{8.57}$$

In region I($x < 0$) the wave function consists of an incident wave of amplitude A and a reflected wave of amplitude B. In region III ($x > a$), there is only a transmitted wave of amplitude F; no reflected wave exists in this region.

In order to obtain the reflection and transmission coefficients, we note that the present problem of scattering by a potential well is mathematically similar to the scattering by a potential barrier. Therefore, without going into the details, we can straightaway write the expressions for the reflection coefficient R and the transmission coefficient T by making the substitution $V_0 \rightarrow -V_0$ and $k' \rightarrow \beta$ in Equations (8.35) and (8.36). We obtain

$$R = \left[1 + \frac{4k^2\beta^2}{(k^2 - \beta^2)^2 \sin^2(\beta a)}\right]^{-1} = \left[1 + \frac{4E(E + V_0)}{V_0^2 \sin^2(\beta a)}\right]^{-1} \tag{8.58}$$

and

$$T = \left[1 + \frac{(k^2 - \beta^2)^2 \sin^2(\beta a)}{4k^2\beta^2}\right]^{-1} = \left[1 + \frac{V_0^2 \sin^2(\beta a)}{4E(E + V_0)}\right]^{-1} \tag{8.59}$$

It can be easily shown that, as expected

$$R + T = 1$$

It may be noted that T is in general less than unity. This is in contradiction to the classical result that the particle should always be transmitted. In order to see the behaviour of T as a function of the particle energy E, we note from Equation (8.59) that $T = 0$ when $E = 0$. As E increases, T oscillates between its maximum value unity and a steadily increasing lower envelope (Figure 8.10). The maxima are obtained when $\beta a = n\pi$ (n = 1,2,....) and minima when $\beta a = (2n + 1)\pi/2$.

As in the case of the potential barrier, perfect transmission takes place when the thickness a of the well is equal to an integral multiple of half the de Broglie wavelength ($2\pi/\beta$) in the internal region.

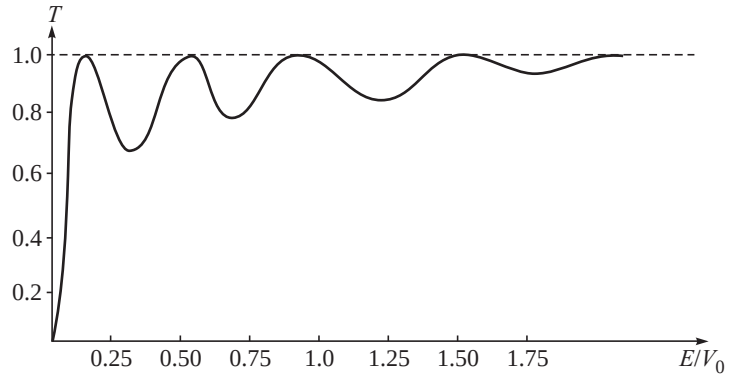

Figure 8.10 Variation of transmission coefficient for a square well as a function of E/V_0 for $(mV_0\, a^2/2\hbar^2)^{1/2} = 10$.

SUMMARY

1. In this chapter we have studied the scattering of a beam of particles of fixed energy E by three simple one-dimensional systems: (a) the potential step, (b) the square barrier, and (c) the square well.

2. The potential step is defined by

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases}$$

***Case* 1: $E > V_0$**

If the beam is incident from the left then the complete eigenfunction is

$$\psi(x) = \begin{cases} \underset{\text{(Incident) (Reflected)}}{Ae^{ikx} + Be^{-ikx}}, & k = \left(\dfrac{2mE}{\hbar^2}\right)^{1/2} & x < 0 \\ \underset{\text{(Transmitted)}}{Ce^{ik'x}}, & k' = \left(\dfrac{2m(E - V_0)}{\hbar^2}\right)^{1/2} & x > 0 \end{cases}$$

The incident beam is partly reflected from the step and partly transmitted to the other side. The reflection and transmission coefficients are, respectively,

$$R = \left[\frac{1 - (1 - V_0/E)^{1/2}}{1 + (1 - V_0/E)^{1/2}}\right]^2$$

and

$$T = \frac{4(1 - V_0/E)^{1/2}}{[1 + (1 - V_0/E)^{1/2}]^2}$$

Also,

$$k(|A|^2 - |B|^2) = k'|C|^2$$

that is, the net current incident from the left is equal to the transmitted current.

***Case* 2: $E < V_0$**

The complete eigenfunction is

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{-Kx}, \quad K = \left(\dfrac{2m(V_0 - E)}{\hbar^2}\right)^{1/2} & x > 0 \end{cases}$$

This shows the wave function is not zero in the region $x > 0$ although it decreases rapidly. Thus, there is nonzero probability of finding the particle in the classically forbidden region. This phenomenon is called

barrier penetration and illustrates a fundamental difference between classical and quantum physics.

However, $R = 1$ and $T = 0$. Thus there is no permanent penetration and all the particles are ultimately returned back.

3. The square barrier is defined by

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 < x < a \\ 0 & x > a \end{cases}$$

***Case* 1: $E > V_0$**

If the beam is incident from the left then the complete eigenfunction is

$$\psi(x) = \begin{cases} \underset{\text{(Incident)}}{Ae^{ikx}} + \underset{\text{(Reflected)}}{Be^{-ikx}} & x < 0 \\ Ce^{ik'x} + De^{-ik'x} & 0 < x < a \\ \underset{\text{(Transmitted)}}{Fe^{ikx}} & x > a \end{cases}$$

The reflection and transmission coefficients are, respectively,

$$R = \left[1 + \frac{4E(E - V_0)}{V_0^2 \sin^2 k'a}\right]^{-1}$$

and

$$T = \left[1 + \frac{V_0^2 \sin^2 k'a}{4E(E - V_0)}\right]^{-1}$$

In general $T < 1$. However, $T = 1$ when the thickness of the barrier is equal to an integral multiple of half the de Broglie wavelength in the internal region.

***Case* 2: $E < V_0$**

The reflection and transmission coefficients are

$$R = \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(Ka)}\right]^{-1}$$

and

$$T = \left[1 + \frac{V_0^2 \sinh^2(Ka)}{4E(V_0 - E)}\right]^{-1}$$

where $$K = \left[\frac{2m(V_0 - E)}{\hbar^2}\right]^{1/2}$$

For a broad high barrier an order-of-magnitude estimate is

$$T \approx e^{-2Ka}$$

Thus the particle has a nonzero probability of passing through a potential barrier which is completely opaque classically. This is called the tunnel effect and is used in explaining various phenomena in atomic, nuclear and solid state physics.

For a variable potential barrier this gives

$$T \approx \exp\left[-\frac{2}{\hbar}\int_{x_1}^{x_2}\sqrt{2m(V(x)-E)}\,dx\right]$$

where x_1 and x_2 are the points for which $V(x) = E$ (classical turning points).

4. The decay of a nucleus by alpha particle emission can be explained on the basis of quantum tunneling. Using the above formula, it is found that the lifetime τ of the alpha particle in the nucleus is given, to a fairly good approximation, by

$$\log \tau = \frac{C_1}{\sqrt{E}} - C_2$$

where E is the energy of the alpha particle and C_1 and C_2 are constants. This formula gives a good fit to the experimental data.

5. The square well is defined by

$$V(x) = \begin{cases} 0 & x < 0 \\ -V_0 & 0 < x < a \\ 0 & x > a \end{cases}$$

If a particle is incident on the well from the left then the complete eigenfunction is

$$\psi(x) = \begin{cases} \underset{\text{(Incident)}}{Ae^{ikx}} + \underset{\text{(Reflected)}}{Be^{-ikx}} & x < 0 \\ Ce^{i\beta x} + De^{-i\beta x}, \quad \beta = \left(\dfrac{2m(E+V_0)}{\hbar^2}\right)^{1/2} & 0 < x < a \\ \underset{\text{(Transmitted)}}{Fe^{ikx}} & x > a \end{cases}$$

The reflection and transmission coefficients are, respectively,

$$R = \left[1 + \frac{4E(E+V_0)}{V_0^2 \sin^2(\beta a)}\right]^{-1}$$

and

$$T = \left[1 + \frac{V_0^2 \sin^2(\beta a)}{4E(E+V_0)}\right]^{-1}$$

T is in general less than unity. Perfect transmission takes place when the thickness a of the well is equal to an integral multiple of half the de Broglie wavelength in the internal region.

QUESTIONS

1. Consider a particle of mass m and energy E approaching, from the left, a one-dimensional potential step given by

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases}$$

Discuss the motion classically and quantum mechanically for the cases (a) $E < V_0$ and (b) $E > V_0$. Obtain the reflection and transmission coefficients.

2. A beam of particles, each of mass m and energy E, is incident on the potential barrier

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 < x < a \\ 0 & x > a \end{cases}$$

(a) Show that there is a nonzero probability of transmission even if $E < V_0$.

(b) Show that for a broad high barrier and $E < V_0$ the transmission coefficient is

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2Ka}, \quad K = \left[\frac{2m(V_0 - E)}{\hbar^2}\right]^{1/2}$$

(c) For $E < V_0$, in the limit $a \to \infty$, show that even though there exists a transmitted wave, the transmission probability current is zero.

3. In Question 2, obtain the reflection and transmission coefficients if $E > V_0$. Show that there is perfect transmission only when the thickness of the barrier is equal to an integral multiple of half the de Broglie wavelength in the internal region.

4. Write a note on the tunnel effect.

5. Explain the alpha decay of a nucleus on the basis of the tunnel effect and obtain an expression for the lifetime of an alpha particle inside the nucleus.

6. Discuss the quantum mechanical scattering of a particle of mass m and energy E by the square potential well

$$V(x) = \begin{cases} 0 & x < 0 \\ -V_0 & 0 < x < a \\ 0 & x > a \end{cases}$$

Obtain the reflection and transmission coefficients and show that their sum is unity.

Show that perfect transmission takes place when the thickness a of the well is equal to an integral multiple of half the de Broglie wavelength in the internal region.

EXERCISES

1. A beam of electrons strikes a potential barrier of height 0.035 eV and infinite width. Calculate the fraction of electrons reflected at the barrier when the energy of the incident electrons is (a) 0.035 eV, (b) 0.020 eV, (c) 0.045 eV. [***Ans.*** (a) 1, (b) 0.13, (c) 1]

2. Electrons of energy 2.0 eV are incident on a potential barrier 4.0 eV high and 0.4 nm wide. Calculate the transmission coefficient.

[***Ans.*** 0.0122]

Chapter

9

The Linear Harmonic Oscillator

Chapter Contents

9.1 The Time-Independent Schrödinger Equation and Its Solution. Energy Eigenvalues
9.2 The Hermite Polynomials
9.3 The Harmonic Oscillator Wave Functions

In this chapter we shall study the one-dimensional motion of a particle attracted to a fixed centre by a force which is proportional to the displacement from that centre. The oscillatory motion that results is called harmonic (or simple harmonic) motion.

The harmonic oscillator is one of the most important and fascinating systems in modern physics. The importance of the harmonic oscillator arises from the fact that more complicated oscillatory motions can be shown to be approximately simple harmonic when the displacement from the equilibrium position is small. It has applications in understanding numerous physical problems, e.g., vibrational motion of nuclei in molecules, theory of radiation, crystal structure etc.

9.1 THE TIME-INDEPENDENT SCHRÖDINGER EQUATION AND ITS SOLUTION. ENERGY EIGENVALUES

The force acting on a particle executing linear harmonic oscillation can be written as

$$F = -kx \tag{9.1}$$

where x is the displacement from the equilibrium position and k is called the force constant. The potential energy corresponding to this force is

$$V(x) = \frac{1}{2} kx^2 \tag{9.2}$$

If ω is the "classical" angular frequency of the oscillator and m is its mass, then

$$\omega = \sqrt{k/m}$$

or $$k = m\omega^2$$

Therefore

$$V(x) = \frac{1}{2} m\omega^2 x^2 \tag{9.3}$$

The time-independent Schrödinger equation for the harmonic oscillator is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi(x) = E\psi(x) \tag{9.4}$$

or $$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2} m\omega^2 x^2\right)\psi(x) = 0$$

or $$\frac{d^2\psi(x)}{dx^2} + \frac{m\omega}{\hbar}\left[\frac{2E}{\hbar\omega} - \frac{m\omega}{\hbar} x^2\right]\psi(x) = 0 \tag{9.5}$$

It is convenient to simplify this equation by introducing the dimensionless eigenvalue

$$\lambda = \frac{2E}{\hbar\omega} \tag{9.6}$$

and the dimensionless variable

$$\xi = \alpha x \tag{9.7}$$

where

$$\alpha = \left(\frac{m\omega}{\hbar}\right)^{1/2} \tag{9.8}$$

We have

$$\frac{d\xi}{dx} = \alpha$$

$$\frac{d\psi}{dx} = \frac{d\psi}{d\xi}\frac{d\xi}{dx} = \alpha\frac{d\psi}{d\xi}$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{d\xi}\left(\frac{d\psi}{dx}\right)\frac{d\xi}{dx}$$

$$= \alpha^2\frac{d^2\psi}{d\xi^2}$$

$$= \frac{m\omega}{\hbar}\frac{d^2\psi}{d\xi^2}$$

Substituting in (9.5),

$$\frac{m\omega}{\hbar}\left[\frac{d^2\psi(\xi)}{d\xi^2}+(\lambda-\xi^2)\,\psi(\xi)\right]=0$$

or
$$\frac{d^2\psi(\xi)}{d\xi^2}+(\lambda-\xi^2)\,\psi(\xi)=0 \tag{9.9}$$

As a first step towards finding acceptable solutions of this equation, we first examine the behaviour of ψ in the asymptotic region $|\xi|\to\infty$. In this limit (9.9) reduces to

$$\frac{d^2\psi(\xi)}{d\xi^2}-\xi^2\psi(\xi)=0 \tag{9.10}$$

It can be easily verified that for large values of $|\xi|$ the functions

$$\psi(\xi)=\xi^n e^{\pm\xi^2/2}$$

n being any constant, satisfy Equation (9.10) so far as the leading terms, which are of order $\xi^2\,\psi(\xi)$, are concerned. Since the wave function must be bounded everywhere, the positive sign in the exponent is not acceptable. This suggests that we should look for exact solution to (9.9) having the form

$$\psi(\xi)=e^{-\xi^2/2}\,H(\xi) \tag{9.11}$$

where $H(\xi)$ are functions which do not affect the required asymptotic behaviour of $\psi(\xi)$. Substituting (9.11) into (9.9) we find that $H(\xi)$ satisfy the *Hermite equation*

$$\frac{d^2H(\xi)}{d\xi^2}-2\xi\frac{dH(\xi)}{d\xi}+(\lambda-1)\,H(\xi)=0 \tag{9.12}$$

This equation can be solved by assuming a power series of the form

$$H(\xi)=\sum_{k=0}^{\infty}a_k\xi^k=a_0+a_1\xi+a_2\xi^2+\ldots \tag{9.13}$$

This gives

$$\frac{dH}{d\xi}=\sum_{k=1}^{\infty}ka_k\,\xi^{k-1}$$

and

$$\frac{d^2H}{d\xi^2}=\sum_{k=2}^{\infty}k(k-1)a_k\,\xi^{k-2}$$

Substituting in Equation (9.12),

$$\sum k(k-1)a_k\xi^{k-2}-2\sum ka_k\xi^k+(\lambda-1)\sum a_k\xi^k=0$$

or $$\sum k(k-1)a_k\xi^{k-2} - \sum (2k - \lambda + 1)\, a_k\, \xi^k = 0$$

For this equation to be satisfied identically for all ξ, the coefficient of each power of ξ must vanish. Setting the coefficient of ξ^k equal to zero, we obtain

$$(k + 2)\,(k + 1)\, a_{k+2} - (2k + 1 - \lambda)a_k = 0$$

or

$$a_{k+2} = \frac{2k+1-\lambda}{(k+2)(k+1)}\, a_k, \quad k = 0,\ 1,\ 2,\ldots \tag{9.14}$$

This equation is called the *recurrence relation*. It shows that all the coefficients can be determined from a_0 and a_1. Thus the general solution of (9.12) has two adjustable parameters. It can be written as the sum of two series, one containing only even powers of q and the other only odd powers:

$$H(\xi) = (a_0 + a_2\xi^2 + a_4\xi^4 + \ldots) + (a_1\xi + a_3\xi^3 + a_5\xi^5 + \ldots) \tag{9.15}$$

Let us now look at the behaviour of this series as $\xi \to \infty$. It is clear that for large ξ, the higher (large k) terms in the series will dominate. Therefore, we examine the behaviour of this series for large k. We have, from (9.14),

$$\frac{a_{k+2}}{a_k} \to \frac{2}{k} \text{ for large } k \tag{9.16}$$

Let us now consider the expansion of the function exp (ξ^2):

$$e^{\xi^2} = \sum_{k=0,2,4,\ldots} b_k\xi^k; \quad b_k = \frac{1}{(k/2)!}$$

The ratio of two consecutive terms is

$$\frac{b_{k+2}}{b_k} = \frac{(k/2)!}{[(k+2)/2]!} = \frac{2}{k+2} \to \frac{2}{k} \text{ for large } k \tag{9.17}$$

Equations (9.16) and (9.17) show that for large k, $H(\xi)$ behaves as exp (ξ^2). Thus, (9.11) shows that for large k,

$$\psi(\xi) \sim e^{\xi^2/2} \tag{9.18}$$

which diverges as $\xi \to \infty$. Therefore, in order to obtain a physically acceptable wave function it is necessary that the series is terminated to a polynomial. The recursion relation (9.14) tells us that this can happen only when λ is an odd integer:

$$\lambda = 2n+1, \qquad n = 0,\ 1,\ 2,\ \ldots \tag{9.19}$$

In that case one of the two series will terminate at $k = n$. The other series is eliminated by setting $a_0 = 0$ if n is odd and $a_1 = 0$ if n is even. In either case, Equations (9.6) and (9.19) yield the **energy eigenvalues**

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \ldots} \tag{9.20}$$

We have labelled the energy eigenvalues by the index n which indicates the degree of the polynomial appearing in the solution.

Note that the infinite sequence of energy levels has the equal spacing $\hbar\omega$ postulated by Planck in 1900. It is also in agreement with the quantization rules of the old quantum theory. However, unlike old quantum theory, the ground state energy is not zero, but is

$$E_0 = \frac{1}{2}\hbar\omega \tag{9.21}$$

This is called the *zero-point energy*. It is characteristic of quantum mechanics and is related to the uncertainty principle. Since the energy is $\frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$, zero energy would be possible only if both p and x vanish simultaneous. This would violate the uncertainty principle.

It may be noted that the eigenvalues (9.20) are *nondegenerate*, because for each value of the quantum number n there exists only one eigenfunction. This is expected because, as we know, the bound states of all one-dimensional systems are nondegenerate.

The potential well and the five lowest energy eigenvalues of the harmonic oscillator are illustrated in Figure 9.1.

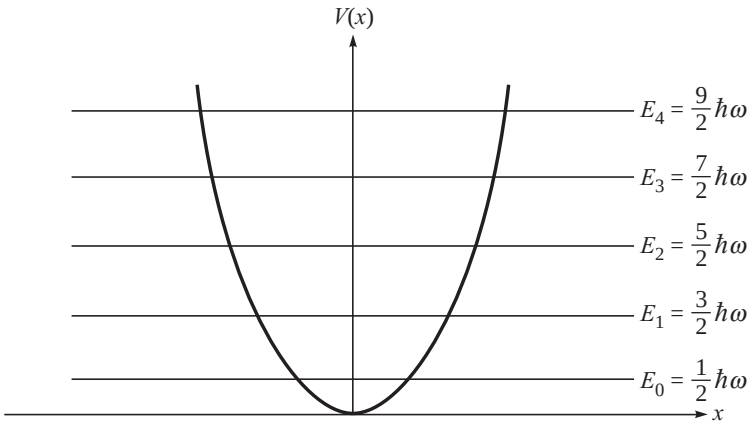

Figure 9.1 The harmonic oscillator potential and its energy levels.

9.2 THE HERMITE POLYNOMIALS

Substituting $\lambda = 2n + 1$ in Equation (9.12),

we get $$H_n''(\xi) - 2\xi H_n'(\xi) + 2n H_n(\xi) = 0 \tag{9.22}$$

The polynomial $H_n(\xi)$ of order n that is a solution of this equation is called the nth *Hermite polynomial*. Their properties are well known and can be found in

most books of mathematical physics†. We record here some important properties which are of interest to us.

Recurrence Relations

$$H_n' = 2nH_{n-1} \tag{9.23a}$$

$$H_{n+1} = 2\xi H_n - 2nH_{n-1} \tag{9.23b}$$

Generating Function

The function

$$G(\xi, s) = e^{-s^2+2s\xi}$$

is called the *generating function* of Hermite polynomials. It can be shown that

$$e^{-s^2+2s\xi} = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n \tag{9.24}$$

Rodrigues' Formula

The Hermite polynomials can be evaluated from the following formula:

$$\boxed{H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} (e^{-\xi^2})} \tag{9.25}$$

The first few Hermite polynomials are:

$$\boxed{\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \\ H_3(\xi) &= 8\xi^3 - 12\xi \\ H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12 \\ H_5(\xi) &= 32\xi^5 - 160\xi^3 + 120\xi \end{aligned}} \tag{9.26}$$

Orthogonality

If $H_n(\xi)$ and $H_m(\xi)$ are Hermite polynomials of orders n and m respectively, then

$$\boxed{\int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi) H_m(\xi) = 0, \quad n \neq m} \tag{9.27}$$

For $n = m$, it can be shown that

$$\boxed{\int_{-\infty}^{\infty} e^{-\xi^2} H_n^2(\xi) d\xi = \sqrt{\pi}\, 2^n n!} \tag{9.28}$$

† See for example, Mathematical Physics by Ghatak et al., Macmillan India Ltd (1995).

9.3 THE HARMONIC OSCILLATOR WAVE FUNCTIONS

Using Equation (9.11) we see that the physically acceptable solutions of Equation (9.9), corresponding to the eigenvalues (9.19) are given by

$$\psi_n(\xi) = e^{-\xi^2/2} H_n(\xi) \tag{9.29}$$

Returning to our original variable x, the eigenfunctions corresponding to the discrete eigenvalues E_n, given by (9.20), can be written as

$$\psi_n(x) = N_n e^{-\alpha^2 x^2/2} H_n(\alpha x), \quad n = 0, 1, 2, \ldots \tag{9.30}$$

where $$\alpha = \sqrt{m\omega/\hbar}$$

The constant N_n can be determined by requiring that the eigenfunctions be normalized to unity. That is,

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = \frac{|N_n|^2}{\alpha} \int_{-\infty}^{\infty} e^{-\xi^2} H_n^2(\xi) \, d\xi = 1 \tag{9.31}$$

Using (9.27) we obtain

$$N_n = \left(\frac{\alpha}{\sqrt{\pi}\, 2^n n!} \right)^{1/2} \tag{9.32}$$

So, the **normalized harmonic oscillator eigenfunctions** are given by

$$\boxed{\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi}\, 2^n n!} \right)^{1/2} e^{-\alpha^2 x^2/2} H_n(\alpha x), \quad n = 0, 1, 2, \ldots} \tag{9.33}$$

From (9.27), we have

$$\int_{-\infty}^{\infty} \psi_n^*(x) \, \psi_m(x) \, dx = 0, \quad n \neq m \tag{9.34}$$

showing that the eigenfunctions are orthogonal. This is in agreement with the fact that the energy eigenvalues are nondegenerate.

We may combine (9.31) and (9.34) by writing

$$\int_{-\infty}^{\infty} \psi_n^*(x) \psi_m(x) \, dx = \delta_{nm} \tag{9.35}$$

showing that the eigenfunctions are **orthonormal**.

The lowest four normalized eigenfunctions are:

$$\left.\begin{aligned}
\psi_0(x) &= \left(\frac{\alpha}{\sqrt{\pi}} \right)^{1/2} \exp\left(-\frac{1}{2} \alpha^2 x^2 \right) \\
\psi_1(x) &= \left(\frac{2\alpha}{\sqrt{\pi}} \right)^{1/2} (\alpha x) \exp\left(-\frac{1}{2} \alpha^2 x^2 \right) \\
\psi_2(x) &= \left(\frac{\alpha}{2\sqrt{\pi}} \right)^{1/2} (2\alpha^2 x^2 - 1) \exp\left(-\frac{1}{2} \alpha^2 x^2 \right) \\
\psi_3(x) &= \left(\frac{\alpha}{3\sqrt{\pi}} \right)^{1/2} (2\alpha^3 x^3 - 3\alpha x) \exp\left(-\frac{1}{2} \alpha^2 x^2 \right)
\end{aligned}\right\} \tag{9.36}$$

These eigenfunctions are plotted in Figure 9.2. The vertical line in each graph represents the amplitude A of a classical harmonic oscillator with the same energy. It is clear that there is some penetration of the wave functions into the regions $|x| > A$ that are forbidden classically. This is similar to the effect that we observed for a particle in a finite square well.

It may be noted that the harmonic oscillator wave functions have a definite *parity*—even when n is zero or even and odd when n is odd.

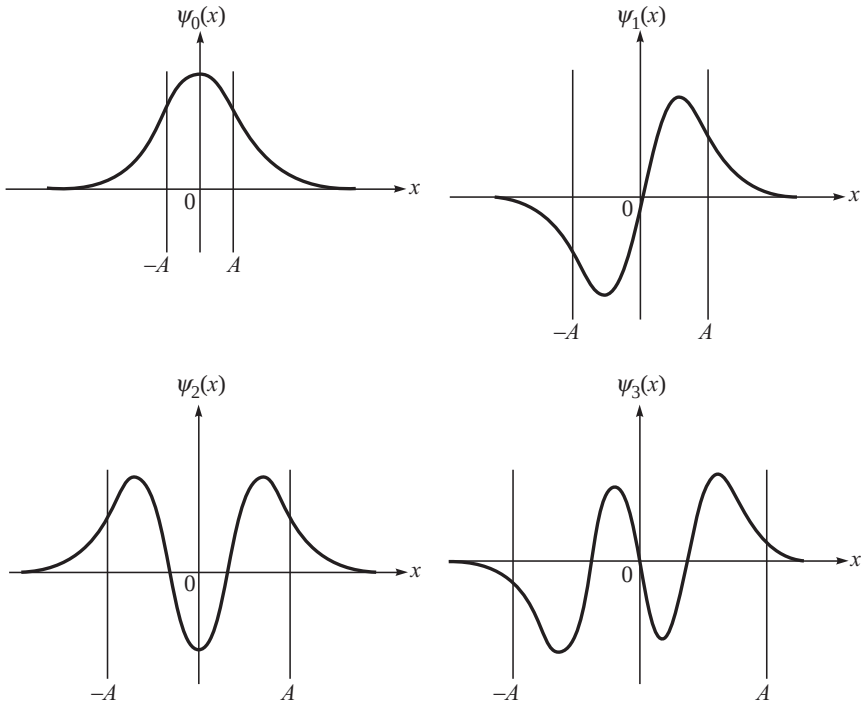

Figure 9.2 The first four harmonic oscillator wave functions, $\psi_n(x)$, $n = 0, 1, 2, 3$. The vertical lines at $x = \pm A$ show the amplitude of a classical oscillator with the same total energy.

Figure 9.3 shows the corresponding position probability densities. Also shown in each case are the probability densities ρ_{cl} for a classical harmonic oscillator (dashed curves). Classically, the probability of finding the particle at a point is inversely proportional to its speed at that point. As such, ρ_{cl} is maximum near the end points of the motion, where the particle moves slowly, and minimum near the equilibrium position, where it moves fast.

It is clear from the figure that for low values of the quantum number n, the quantum mechanical probability densities $|\psi_n(x)|^2$ are quite different from the corresponding classical probability densities ρ_{cl}. In fact, for the lowest energy state $n = 0$, the quantum behaviour is exactly opposite. The probability density $|\psi_0(x)|^2$ has its maximum value at the equilibrium position $x = 0$ and decreases on either side of this position. However, as n increases the disagreement

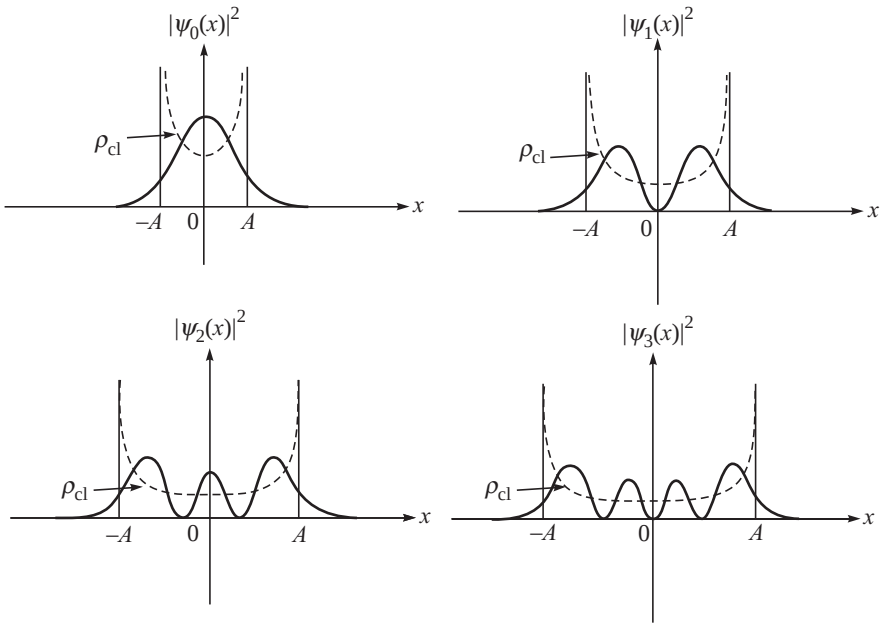

Figure 9.3 Probability densities $|\psi_n(x)|^2$ for the first four harmonic oscillator states. The dotted curves show the corresponding classical probability densities ρ_{cl}.

between the quantum and classical probability densities becomes less and less marked. Figure 9.4 shows the two probability densities for $n = 20$. Note that the general agreement between the two is quite good apart from the rapid fluctuations of the quantum mechanical density. However, the uncertainty principle prevents the detection of these fluctuations when the spacings of the peaks and dips are very small as is the case for large quantum numbers.

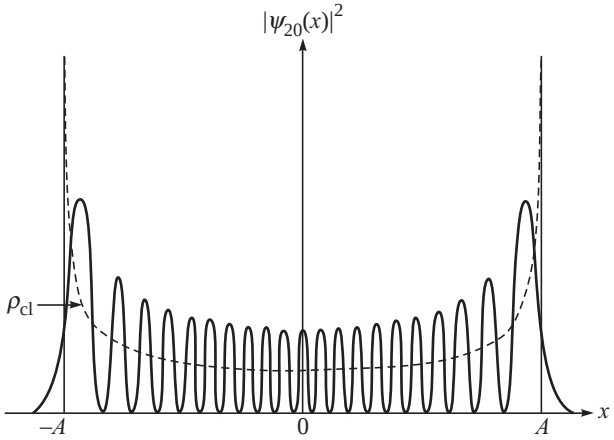

Figure 9.4 Comparison of the Quantum-mechanical and classical probability densities for a harmonic oscillator for the state $n = 20$.

The improved agreement between quantum and classical behaviours as n increases is expected because, for large n, the energy interval is small compared to the total energy. As such, the classical motion is approached wherein the energy is continuous. This is also in accordance with *Bohr's correspondence principle*, which asserts that for large quantum numbers, quantum mechanics gives the same results as classical mechanics.

PROBLEM 9.1 Evaluate (a) $\langle x \rangle$, (b) $\langle x^2 \rangle$, (c) $\langle p \rangle$ and (d) $\langle p^2 \rangle$ for the eigenstates of a harmonic oscillator.

Solution: (a) $\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\, x\, \psi_n(x)\, dx$ (9.37)

We know that the harmonic oscillator wave functions have definite parity. Thus $\psi_n(x)$ is either an even or an odd function of x. Therefore, the product $\psi_n^*(x)\ \psi_n(x)$ will always be even. Since x is odd, the integrand will always be odd and hence $\langle x \rangle = 0$.

For a complete solution from first principles, we proceed as under.

We shall use the recurrence relation (9.23b) for the Hermite polynomials which can be rewritten as

$$2\alpha x H_n(\alpha x) = H_{n+1}(\alpha x) + 2nH_{n-1}(\alpha x) \tag{9.38}$$

The harmonic oscillator wave functions can be written in terms of the Hermite polynomials as

$$\psi_n(x) = \left(\frac{\alpha}{2^n\, n!\sqrt{\pi}}\right)^{1/2} e^{-\alpha^2 x^2/2}\, H_n(\alpha x),\ n = 0,\ 1,\ 2,\ \ldots \tag{9.39}$$

Multiplying Equation (9.38) by

$$\left(\frac{\alpha}{2^n\, n!\sqrt{\pi}}\right)^{1/2} e^{-\alpha^2 x^2/2}$$

and simplifying, we obtain

$$\boxed{x\psi_n(x) = \frac{1}{\alpha\sqrt{2}}\left[\sqrt{n+1}\,\psi_{n+1}(x) + \sqrt{n}\,\psi_{n-1}(x)\right]} \tag{9.40}$$

Substituting in (9.37),

$$\langle x \rangle = \frac{\sqrt{n+1}}{\alpha\sqrt{2}} \int_{-\infty}^{\infty} \psi_n^*(x)\ \psi_{n+1}(x)dx + \frac{\sqrt{n}}{\alpha\sqrt{2}} \int_{-\infty}^{\infty} \psi_n^*(x)\psi_{n-1}(x)dx$$

Since the oscillator wave functions are orthonormal, both the integrals on the right hand side vanish. Therefore,

$$\boxed{\langle x \rangle = 0} \tag{9.41}$$

(b) $\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) x^2 \psi_n(x) dx$

$$= \frac{1}{\sqrt{2}\,\alpha} \int_{-\infty}^{\infty} \psi_n^* \, x \left[\sqrt{n+1}\, \psi_{n+1} + \sqrt{n}\, \psi_{n-1} \right] dx \qquad \text{(using 9.40)}$$

$$= \frac{1}{\sqrt{2}\alpha} \left[\sqrt{n+1} \int_{-\infty}^{\infty} \psi_n^* \, x \, \psi_{n+1} dx + \sqrt{n} \int_{-\infty}^{\infty} \psi_n^* \, x \, \psi_{n-1} dx \right]$$

Using (9.40) again,

$$\langle x^2 \rangle = \frac{1}{\alpha} \sqrt{\frac{n+1}{2}} \left[\int_{-\infty}^{\infty} \psi_n^* \left\{ \frac{1}{\alpha} \sqrt{\frac{n+2}{2}}\, \psi_{n+2} + \frac{1}{\alpha} \sqrt{\frac{n+1}{2}}\, \psi_n \right\} dx \right]$$

$$+ \frac{1}{\alpha} \sqrt{\frac{n}{2}} \left[\int_{-\infty}^{\infty} \psi_n^* \left\{ \frac{1}{\alpha} \sqrt{\frac{n}{2}}\, \psi_n + \frac{1}{\alpha} \sqrt{\frac{n-1}{2}}\, \psi_{n-2} \right\} dx \right]$$

$$= \frac{\sqrt{(n+1)(n+2)}}{2\alpha^2} \int_{-\infty}^{\infty} \psi_n^* \, \psi_{n+2} \, dx + \frac{n+1}{2\alpha^2} \int_{-\infty}^{\infty} \psi_n^* \, \psi_n \, dx$$

$$+ \frac{n}{2\alpha^2} \int \psi_n^* \, \psi_n \, dx + \frac{\sqrt{n(n-1)}}{2\alpha^2} \int_{-\infty}^{\infty} \psi_n^* \, \psi_{n-2} \, dx$$

Using the orthonormality of oscillator wave functions, we obtain

$$\langle x^2 \rangle = \frac{1}{2\alpha^2} \, (n + 1 + n)$$

or

$$\boxed{\langle x^2 \rangle = \frac{2n+1}{2\alpha^2} = \left(n + \frac{1}{2} \right) \frac{\hbar}{m\omega}} \qquad (9.42)$$

(c) $\langle p \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \, \hat{p} \, \psi_n(x) dx$

$$= \int_{-\infty}^{\infty} \psi_n^*(x) \left[-i\hbar \frac{d\psi_n(x)}{dx} \right] dx \qquad (9.43)$$

Now, if $\psi_n(x)$ is odd, then its derivative is even, and vice versa. Therefore, the integrand in the above integral is always an odd function of x. Hence $\langle p \rangle = 0$.

We can also obtain this result using recurrence relation (9.23a):

$$\frac{dH_n(\alpha x)}{d(\alpha x)} = 2n \, H_{n-1}(\alpha x) \qquad (9.44)$$

Differentiating (9.39),

$$\frac{d\psi_n(x)}{dx} = \left(\frac{\alpha}{2^n \, n! \sqrt{\pi}} \right)^{1/2} \times$$

$$\left[-(\alpha^2 x)\exp\left(\frac{-\alpha^2x^2}{2}\right)H_n(\alpha x)+\exp\left(\frac{-\alpha^2x^2}{2}\right)\frac{dH_n(\alpha x)}{dx}\right]$$

$$=-\alpha^2 x\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2}\exp\left(\frac{-\alpha^2x^2}{2}\right)H_n(\alpha x)+\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2}\times$$

$$\alpha\exp\left(\frac{-\alpha^2x^2}{2}\right)\frac{dH_n(\alpha x)}{d(\alpha x)}$$

Using (9.39) and (9.44) this becomes

$$\frac{d\psi_n(x)}{dx}=-\alpha^2x\psi_n(x)+\left(\frac{\alpha}{2^n n!\sqrt{\pi}}\right)^{1/2}\alpha\exp\left(\frac{-\alpha^2x^2}{2}\right)[2nH_{n-1}(\alpha x)]$$

$$=-\alpha^2x\psi_n(x)+(2\alpha n)\frac{1}{\sqrt{2n}}\left(\frac{\alpha}{2^{n-1}(n-1)!\sqrt{\pi}}\right)^{1/2}\exp\left(\frac{-\alpha^2x^2}{2}\right)H_{n-1}(\alpha x)$$

$$=-\alpha^2x\psi_n(x)+2\alpha\left(\frac{n}{2}\right)^{1/2}\psi_{n-1}(x)$$

Using (9.40),

$$\frac{d\psi_n(x)}{dx}=\frac{-\alpha}{\sqrt{2}}[\sqrt{n+1}\,\psi_{n+1}(x)+\sqrt{n}\,\psi_{n-1}(x)]+\frac{2\alpha}{\sqrt{2}}\sqrt{n}\,\psi_{n-1}(x)$$

or
$$\boxed{\frac{d\psi_n(x)}{dx}=\frac{\alpha}{\sqrt{2}}[\sqrt{n}\,\psi_{n-1}(x)-\sqrt{n+1}\,\psi_{n+1}(x)]} \tag{9.45}$$

Substituting in (9.43) and using the orthonormality of eigenfunctions, we get

$$\boxed{\langle p\rangle=0} \tag{9.46}$$

(d) $$\langle p^2\rangle=\int_{-\infty}^{\infty}\psi_n^*(x)\;\hat{p}^2\;\psi_n(x)\,dx$$

$$=-\hbar^2\int_{-\infty}^{\infty}\psi_n^*(x)\;\frac{d^2\psi_n(x)}{dx}\;dx$$

$$=\frac{-\hbar^2\alpha}{\sqrt{2}}\int_{-\infty}^{\infty}\psi_n^*\;\frac{d}{dx}\;[\sqrt{n}\;\psi_{n-1}-\sqrt{n+1}\;\psi_{n+1}]\,dx\;\text{(using 9.45)}$$

$$=\frac{-\hbar^2\alpha}{\sqrt{2}}\left[\sqrt{n}\int_{-\infty}^{\infty}\psi_n^*\frac{d\psi_{n-1}}{dx}\,dx-\sqrt{n+1}\int_{-\infty}^{\infty}\psi_n^*\frac{d\psi_{n+1}}{dx}\,dx\right]$$

Using (9.45) again,

$$\langle p^2\rangle=\frac{-\hbar^2\alpha^2\sqrt{n}}{2}\int_{-\infty}^{\infty}\psi_n^*\,[\sqrt{n-1}\;\;\psi_{n-2}(x)-\sqrt{n}\;\;\psi_n]\,dx$$

$$+ \frac{h^2\alpha^2\sqrt{n+1}}{2}\int_{-\infty}^{\infty}\psi_n^*\,[\sqrt{n+1}\;\;\psi_n - \sqrt{n+2}\;\;\psi_{n+2}]\,dx$$

$$= \frac{-\hbar^2\alpha^2}{2}\left[\sqrt{n(n-1)}\int_{-\infty}^{\infty}\psi_n^*\,\psi_{n-2}\,dx - n\int_{-\infty}^{\infty}\psi_n^*\,\psi_n\,dx\right.$$

$$\left.-(n+1)\int_{-\infty}^{\infty}\psi_n^*\,\psi_n\,dx + \sqrt{(n+1)(n+2)}\int_{-\infty}^{\infty}\psi_n^*\,\psi_{n+2}\,dx\right]$$

Using the orthonormality of oscillator wave function, this reduces to

$$\langle p^2\rangle = -\frac{\hbar^2\alpha^2}{2}(0 - n - (n+1) + 0)$$

$$= \frac{2n+1}{2}\;\;\hbar^2\alpha^2$$

$$= \left(n+\frac{1}{2}\right)\;\hbar^2\left(\frac{m\omega}{\hbar}\right)$$

or
$$\boxed{\langle p^2\rangle = \left(n+\frac{1}{2}\right)m\omega\hbar} \tag{9.47}$$

PROBLEM 9.2 Evaluate the position-momentum uncertainty product for the *n*th state of a linear harmonic oscillator.

Solution:

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2$$

$$\left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega} - 0$$

$$= \left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}$$

$$(\Delta p)^2 = \langle p^2\rangle - \langle p\rangle^2$$

$$= \left(n+\frac{1}{2}\right)\;m\omega\hbar\; - 0 = \left(n+\frac{1}{2}\right)\;m\omega\hbar$$

Multiplying the two and taking square root we obtain the position-momentum uncertainty product

$$\boxed{\Delta x\,\Delta p = \left(n+\frac{1}{2}\right)\hbar, \quad n = 0,1,2,\ldots} \tag{9.48}$$

This is in accordance with the uncertainty relation

$$\Delta x\;\Delta p \geq \frac{\hbar}{2}$$

For $n = 0$, (9.48) reduces to

$$\Delta x \Delta p = \frac{\hbar}{2}$$

showing that *the uncertainty product is minimum for the ground state.*

PROBLEM 9.3 Obtain the expectation values of the kinetic and potential energies for the *n*th state of a linear harmonic oscillator.

Solution: $\langle T \rangle = \frac{1}{2m}\langle p^2 \rangle = \frac{1}{2}\left(n+\frac{1}{2}\right)\hbar\omega = \frac{E_n}{2}$

$$\langle V \rangle = \frac{1}{2}k\langle x^2 \rangle = \frac{1}{2}(m\omega^2)\left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}$$

$$= \frac{1}{2}\left(n+\frac{1}{2}\right)\hbar\omega = \frac{E_n}{2}$$

Thus, the average kinetic and potential energies for a harmonic oscillator in any eigenstate are each equal to one-half the total energy, as in the case of a classical harmonic oscillator.

PROBLEM 9.4 For a linear harmonic oscillator, evaluate

$$x_{kn} = \int_{-\infty}^{\infty} \psi_k^*(x)\, x\, \psi_n(x)\, dx$$

Solution: Consider the recurrence relation (9.40):

$$x\psi_n(x) = \frac{1}{\alpha\sqrt{2}}\left[\sqrt{n+1}\ \psi_{n+1}(x) + \sqrt{n}\ \psi_{n-1}(x)\right]$$

Multiplying by $\psi_k^*(x)$ and integrating over x,

$$\int_{-\infty}^{\infty} \psi_k^*\, x\, \psi_n\, dx = \frac{1}{\alpha\sqrt{2}}\left[\sqrt{n+1}\int_{-\infty}^{\infty}\psi_k^*\,\psi_{n+1}\,dx + \sqrt{n}\int_{-\infty}^{\infty}\psi_k^*\,\psi_{n-1}\,dx\right]$$

Since the oscillator wave functions are orthonormal, the above equation reduces to

$$x_{kn} = \frac{1}{\alpha\sqrt{2}}\left[\sqrt{n+1}\,\delta_{k,n+1} + \sqrt{n}\,\delta_{k,n-1}\right]$$

$$= \sqrt{\frac{(n+1)\hbar}{2m\omega}}\ \delta_{k,n+1} + \sqrt{\frac{n\hbar}{2m\omega}}\ \delta_{k,n-1}$$

Thus,

$$x_{kn} = \begin{cases} \sqrt{\dfrac{(n+1)\hbar}{2m\omega}} & \text{if } k = n+1 \\ \sqrt{\dfrac{n\hbar}{2m\omega}} & \text{if } k = n-1 \\ 0 & \text{otherwise} \end{cases}$$

PROBLEM 9.5 A harmonic oscillator has a wave function which is a superposition of its ground state and first excited state eigenfunctions; that is,

$$\psi(x) = \frac{1}{\sqrt{2}}[\psi_0(x) + \psi_1(x)]$$

Find the expectation value of the energy.

Solution:

$$\langle E \rangle = \int_{-\infty}^{\infty} \psi^*(x)\ \hat{E}\ \psi(x)\ dx$$

$$= \frac{1}{2}\int_{-\infty}^{\infty} [\psi_0^*(x) + \psi_1^*(x)]\ \hat{E}\ [\psi_0(x) + \psi_1(x)]\ dx$$

$$= \frac{1}{2}\left[\int_{-\infty}^{\infty} \psi_0^*(x)\,\hat{E}\,\psi_0(x)\,dx + \int_{-\infty}^{\infty} \psi_1^*(x)\,\hat{E}\,\psi_0(x)\,dx\right.$$

$$\left. + \int_{-\infty}^{\infty} \psi_0^*(x)\,\hat{E}\,\psi_1(x)\,dx + \int_{-\infty}^{\infty} \psi_1^*(x)\,\hat{E}\,\psi_1(x)\,dx\right]$$

$$= \frac{1}{2}\left[E_0\int_{-\infty}^{\infty} \psi_0^*(x)\,\psi_0(x)\,dx + E_0\int_{-\infty}^{\infty} \psi_1^*(x)\,\psi_0(x)\,dx\right.$$

$$\left. + E_1\int_{-\infty}^{\infty} \psi_0^*(x)\,\psi_1(x)\,dx + E_1\int_{-\infty}^{\infty} \psi_1^*(x)\,\psi_1(x)\,dx\right]$$

Since the eigenfunctions are orthonormal, this yields

$$\langle E \rangle = \frac{1}{2}[E_0 + 0 + 0 + E_1]$$

$$= \frac{1}{2}\left[\frac{1}{2}\hbar\omega + \frac{3}{2}\hbar\omega\right] = \boxed{\hbar\omega}$$

PROBLEM 9.6 For a linear harmonic oscillator in its ground state, show that the probability of finding it beyond the classical limits is approximately 0.16.

Solution: The energy of the oscillator in the ground state is

$$E_0 = \frac{1}{2}\hbar\omega$$

Classically, if A is the amplitude of oscillation then the total energy is

$$E_{\text{cl}} = \frac{1}{2}m\omega^2A^2$$

Equating the two,

$$\frac{1}{2}m\omega^2A^2 = \frac{1}{2}\hbar\omega$$

or $$A = \sqrt{\frac{\hbar}{m\omega}} = \frac{1}{\alpha}$$

The ground-state wave function is

$$\psi_0 = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} \exp\left(-\frac{1}{2}\alpha^2 x^2\right)$$

The probability of finding the particle within the classical limits is

$$P_{\text{in}} = \int_{-A}^{A} \psi_0^* \, \psi_0 \, dx$$

$$= \frac{\alpha}{\sqrt{\pi}} \int_{-1/\alpha}^{1/\alpha} e^{-\alpha^2 x^2} \, dx = \frac{2\alpha}{\sqrt{\pi}} \int_0^{1/\alpha} e^{-\alpha^2 x^2} \, dx$$

Let $y = \alpha x$. Then $dy = \alpha dx$. We have

$$P_{\text{in}} = \frac{2}{\sqrt{\pi}} \int_0^1 e^{-y^2} \, dy$$

$$= \frac{2}{\sqrt{\pi}} \int_0^1 \left[1 - y^2 + \frac{y^4}{2!} - \frac{y^6}{3!} + \frac{y^8}{4!} - \ldots\right] dy$$

$$= \frac{2}{\sqrt{\pi}} \left[y - \frac{y^3}{3} + \frac{y^5}{10} - \frac{y^7}{42} + \frac{y^9}{216} - \ldots\right]_0^1$$

$$= \frac{2}{\sqrt{\pi}} \left[1 - \frac{1}{3} + \frac{1}{10} - \frac{1}{42} + \frac{1}{216} - \ldots\right]$$

$$\approx 0.84$$

The probability of finding the particle beyond the classical limits

$$P_{\text{out}} = 1 - P_{\text{in}} = 1 - 0.84 \approx \boxed{0.16}$$

SUMMARY

1. The potential energy of a particle of mass m executing linear harmonic oscillations of angular frequency ω is

$$V(x) = \frac{1}{2} m\omega^2 x^2$$

2. The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi(x) = E\psi(x)$$

3. The energy eigenvalues are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots$$

The energy levels have equal spacing $\hbar\omega$. The ground state energy is not zero; it has the value

$$E_0 = \frac{1}{2}\hbar\omega$$

which is called the zero-point energy.

4. The corresponding normalized eigenfunctions are given by

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi}\,2^n n!}\right)^{1/2} \exp(-\alpha^2x^2/2)H_n(\alpha x), \quad n = 0,1,2, \ldots$$

where $H_n(\alpha x)$ is the nth Hermite polynomial

$$H_n(\xi) = (-1)^n\, e^{\xi^2}\frac{d^n}{d\xi^n}(e^{-\xi^2}); \; \xi = \alpha x, \; \alpha = \left(\frac{m\omega}{\hbar}\right)^{1/2}$$

5. The eigenfunctions have a definite parity—even when n is zero or even and odd when n is odd.

6. For low values of the quantum number n, the quantum mechanical probability densities $|\psi_n(x)|^2$ are quite different from the corresponding classical probability densities. However, as n increases the disagreement between the quantum and classical probability densities becomes less and less marked, in accordance with the correspondence principle.

QUESTIONS

1. Establish the Schrödinger equation for a linear harmonic oscillator and solve it to obtain its eigenvalues and eigenfunctions. Discuss the significance of zero-point energy.

2. Give an outline of the quantum mechanical description of a linear harmonic oscillator. In what way is this description different from the classical description?

3. Sketch the first four wave functions of the linear harmonic oscillator and discuss their parity.

4. Sketch the position probability densities for the first four wave functions of the harmonic oscillator and compare these with the classical probabilities.
In the limit of large n, how does the quantum mechanical result correspond to the classical result?

EXERCISES

1. The energy of a linear harmonic oscillator in the third excited state is 0.1eV. Find the frequency of oscillation. [***Ans.*** 3.3×10^{13} Hz]

2. Substituting the wave function

$$\psi(x) = x \exp(-m\omega x^2/2\hbar)$$

into the Schrödinger equation

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\,(E - V(x))\,\psi(x) = 0$$

where $V = (1/2)\, m\omega^2 x^2$, find the value of E. [***Ans.*** $(3/2)\,\hbar\omega$]

3. The potential energy of a linear harmonic oscillator of mass m, oscillating with angular frequency ω, is $V(x) = (1/2)\, m\omega^2 x^2$.

(a) Write the time-independent Schrödinger equation for the oscillator.

(b) Given the eigenfunction of the Hamiltonian operator for the ground state as

$$\psi_0(x) = (\alpha/\pi)^{1/4} \exp\,(-\alpha x^2/2)$$

where $\alpha = m\omega/\hbar$, calculate the energy eigenvalue for the ground state.

[***Ans.*** (b) $(1/2)\,\hbar\omega$]

4. A particle of mass 1 mg is attached to a spring of spring constant 10^{-3} Nm^{-1}. Calculate its zero point energy. [***Ans.*** 10.4×10^{-15} eV]

Chapter

10 The Formal Structure of Quantum Mechanics

Chapter Contents

10.1 The Dirac Notation
10.2 Operators
10.3 Orthonormal Functions
10.4 Eigenvalues and Eigenfunctions
10.5 The Postulates of Quantum Mechanics
10.6 A Note on the Superposition Principle

We have developed the basic concepts and formulation of quantum mechanics in chapters 4, 5 and 6. The theory was applied successfully to some simple one-dimensional systems in chapters 7, 8 and 9. In this chapter we shall present the basic principles of quantum mechanics as a set of *postulates*. As is true for all fundamental theories, the justification for the postulates lies in logical consistency of the theory developed on them and its success in explaining the experimental results.

The postulates are presented in different books in somewhat different ways. Even the ordering and the total number of postulates are quite arbitrary because some books combine two postulates in a single statement. However, all the books present the same basic ideas as postulates of quantum mechanics.

Before stating the postulates, we shall review the general properties of operators and their eigenvalues and eigenfunctions. We shall use the terms "system" and "particle" interchangeably, since a single particle is the simplest quantum mechanical system.

10.1 THE DIRAC NOTATION

In this section we introduce the *Dirac notation*, which is a very convenient and compact notation for the scalar product of two functions. The **scalar product**

of two functions $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ is denoted by the symbol $\langle\psi_1|\psi_2\rangle$:

$$\boxed{\langle\psi_1|\psi_2\rangle = \int \psi_1^*(\mathbf{r})\psi_2(\mathbf{r})d\mathbf{r}} \quad \textbf{(Dirac notation)} \tag{10.1}$$

The object $|\psi_2\rangle$ is known as a *ket* vector while $\langle\psi_1|$ is known as a *bra* vector. They join together to form the "bra-ket" $\langle\psi_1|\psi_2\rangle$. From the definition (10.1) we have

$$\langle\psi_2|\psi_1\rangle = \langle\psi_1|\psi_2\rangle^* \tag{10.2a}$$

$$\langle\psi_1|c\psi_2\rangle = c\langle\psi_1|\psi_2\rangle \tag{10.2b}$$

$$\langle c\psi_1|\psi_2\rangle = c^*\langle\psi_1|\psi_2\rangle \tag{10.2c}$$

$$\langle\psi_3|\psi_1+\psi_2\rangle = \langle\psi_3|\psi_1\rangle + \langle\psi_3|\psi_2\rangle \tag{10.2d}$$

where c is a complex number and ψ_3 is a third function.

10.2 OPERATORS

An operator transforms one function into another. If an operator A transforms the function ψ into the function ϕ, then we write

$$A\psi = \phi \tag{10.3}$$

For example,

$$A\psi(x) = x\psi(x) \tag{10.4}$$

indicates that the operator A multiplies the function $\psi(x)$ by x. Similarly,

$$A\psi(x) = \frac{d}{dx}\psi(x) \tag{10.5}$$

means that the operator A differentiates the function $\psi(x)$.

An operator A is said to be **linear** if it satisfies

$$A[\psi_1 + \psi_2] = A\psi_1 + A\psi_2 \tag{10.6}$$

and

$$A[c\psi] = cA\psi \tag{10.7}$$

where c is a constant. These two conditions are equivalent to the single condition

$$\boxed{A[c_1\psi_1 + c_2\psi_2] = c_1A\psi_1 + c_2A\psi_2} \quad \textbf{(Condition for linearity)} \tag{10.8}$$

It can be easily shown that the operator d/dx is linear. In fact, all the operators used in quantum mechanics are linear.

Hermitian Operator

An operator A is said to be Hermitian if it satisfies

$$\boxed{\langle \psi_1 | A\psi_2 \rangle = \langle A\psi_1 | \psi_2 \rangle \quad \textbf{(Hermitian operator)}} \tag{10.9}$$

for any two functions ψ_1 and ψ_2 of the function space on which the operator A acts.

The importance of Hermitian operators in quantum mechanics will be clear very soon.

PROBLEM 10.1 Prove that the momentum operator $-i\hbar\nabla$ is Hermitian.

Solution: For the momentum operator to be Hermitian,

$$\int \psi^*(-i\hbar\nabla\psi)\,d\mathbf{r} = \int (-i\hbar\nabla\psi)^*\,\psi\,d\mathbf{r}$$

or
$$-i\hbar\int \psi^*\nabla\psi\,d\mathbf{r} = i\hbar\int (\nabla\psi^*)\,\psi\,d\mathbf{r}$$

or
$$\int \psi^*\nabla\psi\,d\mathbf{r} = -\int (\nabla\psi^*)\psi\,d\mathbf{r}$$

Now, integrating the left-hand integral by parts,

$$\int \psi^*\nabla\psi\,d\mathbf{r} = \psi^*\psi\Big|_{-\infty}^{\infty} - \int (\nabla\psi^*)\psi\,d\mathbf{r}$$

Since ψ vanishes at infinity, the first term on the right is zero. Hence it is proved that the momentum operator is Hermitian.

Commutator

The commutator of the operators A and B, denoted as $[A, B]$, is defined as

$$\boxed{[A, B] = AB - BA \quad \textbf{(Commutator of A and B)}} \tag{10.10}$$

It follows that

$$[B, A] = -[A, B] \tag{10.11}$$

If $[A, B] = 0$, that is, if $AB = BA$, the operators A and B are said to *commute.* If $AB \neq BA$, we say that the operators do not commute.

PROBLEM 10.2 Find the value of the commutator $\left[x, \dfrac{d}{dx}\right]$.

Solution: We have for any function $\psi(x)$

$$\left[x, \frac{d}{dx}\right]\psi(x) = \left(x\frac{d}{dx} - \frac{d}{dx}x\right)\psi(x)$$

$$= x\frac{d\psi}{dx} - \frac{d}{dx}(x\psi)$$
$$= x\frac{d\psi}{dx} - x\frac{d\psi}{dx} - \psi(x)$$
$$= -\psi(x)$$

Since $\psi(x)$ is arbitrary, this gives

$$\left[x, \frac{d}{dx}\right] = -1$$

PROBLEM 10.3 Prove the following commutator relations

(a) $[A, B + C] = [A, B] + [A, C]$
(b) $[A, BC] = [A, B]C + B[A, C]$
(c) Jacobi identity: $[A, [B, C] + [B, [C, A]] + [C, [A, B]] = 0$

Solution: (a) $[A, B + C] = A(B + C) - (B + C)A$
$= AB + AC - BA - CA$
$= AB - BA + AC - CA$
$= [A, B] + [A, C]$

(b) $[A, BC] = ABC - BCA$
$= ABC - BCA + BAC - BAC$
$= ABC - BAC + BAC - BCA$
$= (AB - BA)C + B(AC - CA)$
$= [A, B]\ C + B[A, C]$

(c) Expand all commutators and add.

10.3 ORTHONORMAL FUNCTIONS

Consider two nonzero functions ψ_i and ψ_j. The functions are said to be **orthogonal** if their scalar product is zero:

$$\boxed{\langle \psi_i | \psi_j \rangle = 0 \quad \textbf{(Orthogonality condition)}} \tag{10.12}$$

A function is said to be **normalized** if the scalar product of a function with itself is unity:

$$\boxed{\langle \psi | \psi \rangle = \int |\psi^2| \, d\mathbf{r} = 1 \quad \textbf{(Normalized function)}} \tag{10.13}$$

A set of normalized functions which are orthogonal to one another are said to form an **orthonormal set.** The *orthonormality condition* is

$$\boxed{\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \textbf{(Orthonormality condition)}} \tag{10.14}$$

where the Kronecker symbol $\delta_{ij} = 1$ for $i = j$ and zero for $i \neq j$.

10.4 EIGENVALUES AND EIGENFUNCTIONS

If the result of applying an operator A on a wave function ψ is a scalar multiple of ψ itself, that is,

$$A\psi = \lambda\psi \tag{10.15}$$

where λ is a complex number, then ψ is called an **eigenfunction** of A and λ is called the corresponding **eigenvalue**.

If there is a whole set of eigenfunctions ψ_n of an operator A, there is an eigenvalue λ_n associated with each eigenfunction. Thus,

$$\boxed{\begin{array}{c} A\psi_n = \lambda_n \psi_n \\ \textbf{(Eigenvalue equation)} \end{array}} \tag{10.16}$$

where n takes integral values. For example, the function $\psi_n = \sin nx$ is an eigenfunction of the operator d^2/dx^2 with the eigenvalue $-n^2$.

$$\frac{d^2}{dx^2}(\sin nx) = n\frac{d}{dx}(\cos nx) = -n^2 (\sin nx)$$

Equation (10.16) is called an eigenvalues equation.

The number of eigenvalues and eigenfunctions of a quantum mechanical operator is, in general, infinite. The totality of all the eigenvalues of an operator is called the *spectrum* of the operator. This may be discrete, continuous or partly discrete and partly continuous.

Degeneracy

If more than one linearly independent eigenfunction have the same eigenvalue, then this eigenvalue is said to be *degenerate.*

One of the main occupations of quantum mechanics is that of solving an eigenvalue equation when only the operator A is known. For example, the time-independent Schrödinger equation [see (6.65)]

$$H\psi_n = E_n\psi_n \tag{10.17}$$

is an energy eigenvalue equation with the Hamiltonian operator given by

$$H = -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r}) \tag{10.18}$$

Another important example is that of finding the eigenvalues and eigenfunctions of the angular momentum operators, which we shall study in chapter 11.

We shall now prove two important theorems concerning eigenvalues and eigenvectors of Hermitian operators.

THEOREM 10.1 The eigenvalues of a Hermitian operator are real.

Proof: We have

$$A\psi = \lambda\psi$$

Since A is Hermitian,

$$\langle \psi | A\psi \rangle = \langle A\psi | \psi \rangle$$

or $$\langle \psi | \lambda\psi \rangle = \langle \lambda\psi | \psi \rangle$$

or $$\lambda \langle \psi | \psi \rangle = \lambda^* \langle \psi | \psi \rangle$$

or $$(\lambda - \lambda^*) \langle \psi | \psi \rangle = 0$$

Since $\langle \psi | \psi \rangle \neq 0$, we obtain

$$\lambda^* = \lambda$$

Hence the eigenvalue λ is real.

THEOREM 10.2 The eigenfunctions of a Hermitian operator corresponding to distinct eigenvalues are orthogonal.

Proof: Let ψ_1 and ψ_2 be two eigenfunctions of a Hermitian operator A and let λ_1 and λ_2 be the respective eigenvalues. Then,

$$A\psi_1 = \lambda_1 \psi_1$$
$$A\psi_2 = \lambda_2 \psi_2$$

Since A is Hermitian, we have

$$\langle \psi_2 | A\psi_1 \rangle = \langle A\psi_2 | \psi_1 \rangle$$

or $$\langle \psi_2 | \lambda_1 \psi_1 \rangle = \langle \lambda_2 \psi_2 | \psi_1 \rangle$$

or $$\lambda_1 \langle \psi_2 | \psi_1 \rangle = \lambda_2^* \langle \psi_2 | \psi_1 \rangle$$

Since $\lambda_2^* = \lambda_2$, this gives

$$(\lambda_1 - \lambda_2) \langle \psi_2 | \psi_1 \rangle = 0$$

Since $\lambda_1 \neq \lambda_2$, we obtain

$$\langle \psi_2 | \psi_1 \rangle = 0$$

Thus ψ_1 and ψ_2 are orthogonal.

If an eigenvalue is degenerate, then the corresponding eigenfunctions are not necessarily orthogonal. However, it is possible to construct a new set of mutually orthogonal eigenfunctions using the Schmidt orthogonalization procedure. We shall not discuss this[†].

Eigenfunctions of Commuting Operators

THEOREM 10.3 If two operators commute, they have common set of eigenfunctions.

Proof: We shall prove the theorem only for the case of *nondegenerate* eigenvalues.

Let A and B be two commuting operators, that is,

$$AB = BA$$

[†] Interested readers may consult Quantum Mechanics by E. Merzbacher.

Let ψ be an eigenfunction of A and let a be the corresponding eigenvalue:

$$A\psi = a\psi$$

Then

$$A(B\psi) = BA\psi = B(a\psi) = a(B\psi)$$

This shows that $B\psi$ is an eigenfunction of A corresponding to the eigenvalue a. Since a is nondegenerate, $B\psi$ can differ from ψ only by a multiplicative constant, say b. That is,

$$B\psi = b\psi$$

Thus, ψ is an eigenfunction of B, having eigenvalue b.

Hence ψ is simultaneously an eigenfunction of both the operators A and B with the eigenvalues a and b, respectively.

The **converse** of this theorem is also true, i.e., *if two operators have common set of eigenfunctions, they commute.*

10.5 THE POSTULATES OF QUANTUM MECHANICS

Postulate 1: The Wave Function

The dynamical state of a physical system may be represented by a wave function (or a state function) which contains all the information that can be known about the state of the system. The function is continuous and differentiable. It is, in general, complex and may be multiplied by any complex number without affecting its physical significance.

Let $\Psi(\mathbf{r}, t)$ be the wave function associated with a particle. Since the wave function is arbitrary to within a multiplicative constant, it is convenient to choose this constant so that the wave function is normalized:

$$\int |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1 \tag{10.19}$$

where the integral extends over all space.

The quantity

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 \tag{10.20}$$

can be interpreted as *position probability density.* That is, the probability of finding the particle, at time t, within the volume element $d\mathbf{r} = dx\, dy\, dz$ about the point $\mathbf{r} = (x, y, z)$ is

$$P(\mathbf{r}, t)d\mathbf{r} = |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)d\mathbf{r} \tag{10.21}$$

This is the **statistical interpretation of the wave function,** first suggested by Max Born.

There are some wave functions, such as plane waves, which are not square integrable, i.e., for which the integral in Equation (10.19) does not exist. Normalization of such functions is done either by enclosing the system in a large box or by using the Dirac delta function (see section 6.9).

Postulate 2: The Superposition Principle

According to the superposition principle, if the wave functions $\Psi_1, \Psi_2, \ldots, \Psi_n$ are associated with possible states of a physical system, then any linear combination

$$\Psi = \sum_{i=1}^{n} c_i \Psi_i \tag{10.22}$$

where the c_i are complex constants, is also a wave function associated with a possible state of the system.

The reader may recall that the superposition principle underlies the representation of a particle by a wave packet which is formed by superposition of plane waves (see Equation 5.5).

Postulate 3: Operators

With every physical observable (or dynamical variable) is associated a linear, Hermitian operator.

The rule for associating a linear operator with a dynamical variable (already discussed in section 6.4) is as follows:

Let $A(\mathbf{r}, \mathbf{p}, t)$ be a dynamical variable representing a physical quantity associated with a particle. We obtain the corresponding operator $\hat{A}(\mathbf{r}, -i\hbar\nabla, t)$ by performing the substitutions

$$\boxed{\begin{aligned} \mathbf{r} &\rightarrow \mathbf{r} \\ \mathbf{p} &\rightarrow -i\hbar\nabla \end{aligned}} \tag{10.23}$$

Postulate 4: Expansion in Eigenfunctions

All the eigenfunctions of any physical observable A constitute a *complete set of functions* so that a wave function representing any state of the system can be expressed as a linear combination of the eigenfunctions of the corresponding operator $\hat{A}$. If all the eigenvalues are discrete, then

$$\Psi = \sum c_n \psi_n \tag{10.24}$$

where ψ_n are the eigenfunctions of $\hat{A}$.

Postulate 5: Measurement of an Observable: Eigenvalues

The only possible result of a *measurement* of the observable A is one of the eigenvalues of the operator $\hat{A}$ associated with A.

Since the results of measurements are real numbers, a Hermitian operator is suitable to represent physical observables.

If the wave function of a system is simply one of the eigenfunctions of the operator $\hat{A}$, having the eigenvalue λ_n, then a measurement of the observable A will certainly yield the result λ_n. However, if the wave function is not an eigenfunction of $\hat{A}$, then a measurement of A will yield any one of the values

$\lambda_1, \lambda_2, \ldots$. Thus, the act of measurement forces the system into one of its eigenstates. It is not possible to predict which eigenstate the system will change into. However, it is possible to find the probability of obtaining a particular eigenvalue λ_n. We shall see this after the next postulate.

Postulate 6: Expectation Values

If a system is described by a normalized wave function Ψ, the *expectation value* of a measurement of an observable A is given by

$$\boxed{\langle A \rangle = \langle \psi | A\psi \rangle \quad \textbf{(Expectation value)}} \tag{10.25}$$

We have $$\langle A \rangle^* = \langle \psi | A\psi \rangle^* = \langle A\psi | \psi \rangle$$

Since $\hat{A}$ is Hermitian,

$$\langle A\psi | \psi \rangle = \langle \psi | A\psi \rangle$$

It follows that $\langle A \rangle^* = \langle A \rangle$. That is, $\langle A \rangle$ is real.

The expectation value may be interpreted as either the average value of the same measurement of the quantity A on many identical systems or the average value of many measurements on the same system.

Expanding Ψ in terms of ψ_n as in (10.24),

$$\langle A \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | A\psi_n \rangle$$

$$= \sum_m \sum_n c_m^* c_n \lambda_n \langle \psi_m | \psi_n \rangle$$

If the eigenfunctions ψ_n are orthonormal, then

$$\langle \psi_m | \psi_n \rangle = \delta_{mn}$$

So,

$$\langle A \rangle = \sum_m \sum_n c_m^* c_n \lambda_n \delta_{mn}$$

$$= \sum_n |c_n|^2 \lambda_n \tag{10.26}$$

Since Ψ is normalized, that is,

$$\langle \Psi | \Psi \rangle = 1$$

we also have

$$\sum_n |c_n|^2 = 1 \tag{10.27}$$

Equation (10.26) shows that the expectation value is the *weighted average of all the eigenvalues of* $\hat{A}$. Of course, a single measurement will always yield

just one of the eigenvalues of $\hat{A}$. Following Born's interpretation, we call the quantity

$$P_n = |c_n|^2 \tag{10.28}$$

the *probability* that a given measurement will yield the particular eigenvalue λ_n. The condition (10.27) expresses the fact that the total probability is unity.

Postulate 7: Time Development of the Wave Function

The wave function of a system develops in time according the **time-dependent Schrödinger equation**

$$\boxed{i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = H \Psi(\mathbf{r}, t)} \tag{10.29}$$

when H is the Hamiltonian operator for the system. For a single particle of mass m, having potential energy $V(\mathbf{r}, t)$, the Hamiltonian is given by

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}, t) \tag{10.30}$$

If the potential is time-independent, i.e., $V(\mathbf{r}, t) = V(\mathbf{r})$, then $\Psi(\mathbf{r}, t)$ may be written as the product of a spatial function $\psi(\mathbf{r})$ and a time function $f(t)$. The spatial part is an energy eigenfunction satisfying the eigenvalue equation

$$H \psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r}) \tag{10.31}$$

where E_n is the energy of the nth state. Since E_n remains constant in time, the solution ψ_n are called *stationary states*. They form a complete, orthonormal set of functions. The solutions of (10.29) can then be written as

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})\, e^{-iE_n t/\hbar} \tag{10.32}$$

According to the superposition principle, the general solution of (10.29) may be written as

$$\Psi(\mathbf{r}, t) = \sum_n c_n \psi_n(\mathbf{r})\, e^{-iE_n t/\hbar} \tag{10.33}$$

10.6 A NOTE ON THE SUPERPOSITION PRINCIPLE

The principle of superposition of states (Postulate 2) is one of the most fundamental concepts of quantum mechanics. It states that the wave functions representing the states of a quantum mechanical system can be superposed linearly to form new wave functions which also represent possible states of the same system. A proper understanding of this principle is very important in order to have a working knowledge of quantum theory. However, it is not easy for the beginner to comprehend this principle and therefore he/she should not get disheartened if the first encounter with this principle leads to confusion and misconception.

Perhaps the main reason for the confusion is that there is no superposition of states in classical physics, even though the concept of superposition occurs quite frequently therein, the most well known being the superposition of waves. Mathematically, the classical and quantum superpositions appear to be analogous. However, this analogy is misleading. As Dirac writes in his classic book[†], *"The assumption of superposition relationships between the states leads to a mathematical theory in which the equations that define a state are linear in the unknowns. In consequence of this, people have tried to establish analogies with systems in classical mechanics, such as vibrating strings or membranes, which are governed by linear equations and for which, therefore, a superposition principle holds. It is important to remember, however, that the superposition that occurs in quantum mechanics is of an essentially different nature from any occurring in the classical theory, as is shown by the fact that the quantum superposition principle demands indeterminacy in the result of observations."*

It may be noted that Postulate 4 concerning expansion of a wavefunction representing any state of a system in terms of the eigenfunctions of an operator is a consequence of the superposition principle.

A particularly common and serious misconception in the minds of the beginner is that "*the energy eigenstates are the only allowed states*[††]". It seems to arise partly from the statement that "*the energy eigenvalues are the only allowed energies*", which is correct.

This misconception is clarified if one understands the relationship between the superposition principle and the measurement process (see Postulate 5). Suppose a dynamical variable of a system is to be measured in an experiment. Let Ψ_1 and Ψ_2 be two states of the system such that if an observation is made in state Ψ_1, one gets the definite result λ_1, and if the observation is made in state Ψ_2, the result is definitely λ_2. The crucial question now is: What will be the result of the observation if the system is in the superposed state $\Psi = c_1\Psi_1 + c_2\Psi_2$. The answer is: The result will sometimes be λ_1 and sometimes λ_2. No other result will ever be obtained. However, it cannot be predicted when we would get the result λ_1 and when we would get λ_2. We can only say that the *probability* of getting result λ_1 is $|c_1|^2$ and the probability of getting λ_2 is $|c_2|^2$.

The reader will recall from section 4.4 that the interference effects in the double-slit experiment can be explained only by using the superposition principle. It can be shown that the superposition principles also makes it possible to obtain a deeper understanding of the uncertainty principle. However, we shall not discussion it here.

[†] P.A.M. Dirac: The Principle of Quantum Mechanics, 4th edition, Oxford University Press, New York (1958).

[††] See Daniel F Styer, *Common Misconceptions Regarding Quantum Mechanics*, Am.J. Phys. 64(1), 1996.

Chapter

Orbital Angular Momentum in Quantum Mechanics

11

Chapter Contents

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So far, we have mainly concentrated on the application of quantum mechanics to systems in one dimension. We shall now study the application of quantum mechanics to some simple three-dimensional systems. An important new concept that now appears is that of angular momentum. We have already encountered this in the discussion of the Bohr model.

We know that in classical mechanics, the angular momentum is one of the three fundamental constants of motion of an isolated system, the other two being energy and linear momentum. It turns out that this statement is also true for isolated quantum mechanical systems. The correspondence principle also demands that this must be so. The conservation of angular momentum is actually a consequence of the *isotropy of space*, which means that the physical laws governing an isolated system do not depend on the orientation of that system in space.

In this chapter we shall consider *orbital* angular momentum, which is the counterpart of the angular momentum encountered in classical physics. We shall see later (in chapter 13) that in quantum mechanics the angular momentum is a more general concept. In addition to orbital angular momentum, there is an

intrinsic property of elementary particles which is called *spin* angular momentum. It has no classical counterpart. The total angular momentum of a particle is the vector sum of the orbital and spin angular momenta.

11.1 THE ORBITAL ANGULAR MOMENTUM OPERATOR AND ITS CARTESIAN COMPONENTS

Classically, the angular momentum **L** of a particle with respect to some fixed origin *O* is defined as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{11.1}$$

where **p** is the momentum of the particle and **r** is its position vector with respect to *O*. Thus **L** is a vector which points in a direction at right angles to the plane containing **r** and **p**. The Cartesian components of **L** are

$$L_x = yp_z - zp_y \tag{11.2a}$$
$$L_y = zp_x - xp_z \tag{11.2b}$$
$$L_z = xp_y - yp_x \tag{11.2c}$$

The corresponding quantum mechanical operators are obtained by replacing **p**, p_x, p_y and p_z by the respective operators representing them. We have

$$\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla) \tag{11.3}$$

and

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{11.4a}$$
$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{11.4b}$$
$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{11.4c}$$

(Angular momentum operators)

11.2 COMMUTATION RELATIONS

Let us now obtain the commutation relations between L_x, L_y and L_z. For this we use the basic commutation relations between position and momentum operators, viz.,

$$[x, p_x] = [y, p_y] = [z, p_z] = i\hbar$$

with all other pairs (for example x and p_y) commuting. We have

$$\begin{aligned}[L_x, L_y] &= L_x L_y - L_y L_x \\ &= (yp_z - zp_y)(zp_x - xp_z) - (zp_x - xp_z)(yp_z - zp_y) \\ &= yp_z zp_x - yp_z xp_z - zp_y zp_x + zp_y xp_z - zp_x yp_z \\ &\quad + zp_x zp_y + xp_z yp_z - xp_z zp_y\end{aligned}$$

$$= yp_x(p_z z - zp_z) + p_y x(zp_z - p_z z)$$
$$= (zp_z - p_z z)\ (xp_y - yp_x)$$
$$= [z,\ p_z]\ (xp_y - yp_x)$$
$$= i\hbar L_z$$

In similar fashion we obtain the values of the commutators $[L_y,\ L_z]$ and $[L_z,\ L_x]$. Putting all the three together, we have

$$[L_x, L_y] = i\hbar L_z \quad (11.5a)$$
$$[L_y, L_z] = i\hbar L_x \quad (11.5b)$$
$$[L_z, L_x] = i\hbar L_y \quad (11.5c)$$

(Commutation relations)

We find that the operators representing any two components of the orbital angular momentum do not commute. As discussed in chapter 10, it implies that they cannot have simultaneous eigenfunctions and hence cannot be precisely measured simultaneously. As such, it is, in general, impossible to assign definite values to all the components simultaneously. In other words, if a system of particles is in an eigenstate of one of the components, it cannot be in an eigenstate of either of the other two components.

Let us now consider the operator representing the square of the magnitude of the orbital angular momentum:

$$L^2 = L_x^2 + L_y^2 + L_z^2 \quad (11.6)$$

Let us evaluate its commutator with L_x:

$$[L^2,\ L_x] = [L_x^2 + L_y^2 + L_z^2,\ L_x]$$

Since $[L_x^2,\ L_x] = 0$, we get

$$[L^2,\ L_x] = [L_y^2,\ L_x] + [L_z^2,\ L_x]$$
$$= L_y[L_y,\ L_x] + [L_y,\ L_x]L_y + L_z[L_z,\ L_x] + [L_z,\ L_x]L_z$$
$$= -i\hbar(L_y\ L_z + L_z\ L_y) + i\hbar(L_z\ L_y + L_y\ L_z)$$
$$= 0$$

In a similar manner, we can show that L_y and L_z also commute with L^2. Thus,

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0 \quad (11.7)$$

This shows that the magnitude of the orbital angular momentum and any one of its Cartesian components can be simultaneously measured precisely. Therefore, it is possible to find simultaneous eigenfunctions of L^2 and any one of L_x, L_y or L_z.

11.3 ANGULAR MOMENTUM OPERATORS IN SPHERICAL POLAR COORDINATES

In order to obtain the eigenvalues and simultaneous eigenfunctions of L^2 and one of the components of **L**, it is convenient to express the operators in spherical polar coordinates (r, θ, ϕ). As shown in Figure 11.1, the spherical and Cartesian coordinates of a point P are related as

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned} \tag{11.8}$$

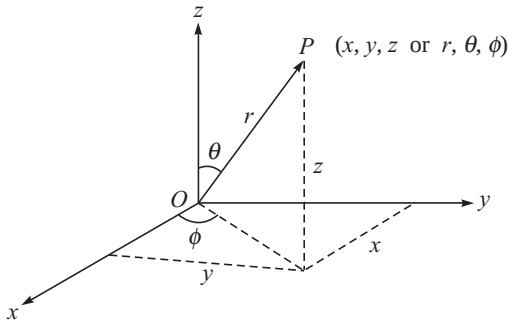


Figure 11.1 The Cartesian and spherical polar coordinates of a point P. **OP** = **r** is the position vector of P with respect to the origin.

with $0 \le r \le \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$. After some straightforward but lengthy algebra, it can be shown that

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{11.9a}$$

$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \tag{11.9b}$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi} \tag{11.9c}$$

and

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{11.10}$$

11.4 EIGENVALUES AND EIGENFUNCTIONS OF L^2 AND L_z

From (11.9) we note that the expression for L_z is simpler than those for L_x and L_y. Therefore, it is convenient to obtain simultaneous eigenfunctions of L^2 and L_z.

Let us denote the eigenvalues of L^2 and L_z by $\lambda\hbar^2$ and $m_l\hbar$, respectively, and let the corresponding common eigenfunction be $Y(\theta, \phi)$. Then the two eigenvalue equations can be written as

$$L^2Y(\theta, \phi) = \lambda\hbar^2 Y(\theta, \phi) \tag{11.11}$$

and

$$L_zY(\theta, \phi) = m_l\hbar\, Y(\theta, \phi) \tag{11.12}$$

The subscript l is attached to m for later convenience. Substituting for L^2 from (11.10) into (11.11), we obtain

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + \lambda Y = 0 \tag{11.13}$$

This equation can be solved by using the method of separation of variables. We write

$$Y(\theta, \phi) = \Theta(\theta)\ \Phi(\phi) \tag{11.14}$$

Substituting in (11.13), multiplying by $\sin^2\theta/Y(\theta, \phi)$ and rearranging, we obtain

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \frac{\sin^2\theta}{\Theta}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta} + \lambda\Theta\right)\right]$$

The variables have separated out, and therefore, each side must be equal to a constant. We take this constant to be m_l^2 for reason which will become clear soon and obtain the following ordinary differential equations:

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\,\Phi = 0 \tag{11.15}$$

and

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m_l^2}{\sin^2\theta}\right)\Theta = 0 \tag{11.16}$$

Equation (11.15) can be immediately solved to give

$$\Phi(\phi) = Ae^{im_l\phi}$$

where A is an arbitrary constant. For $\Phi(\phi)$ to be single-valued we must have

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

or $$e^{2\pi m_l i} = 1$$

or $$m_l = 0, \pm1, \pm2, \ldots$$

Taking $A = 1/\sqrt{2\pi}$, we obtain the normalized solutions of (11.15):

$$\boxed{\Phi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}; \qquad m_l = 0, \pm1, \pm2, \ldots} \tag{11.17}$$

where we have labelled the functions by the subscript m_l. It can be easily shown that these functions form an orthonormal set. That is,

$$\int_0^{2\pi} \Phi^*_{m'_l}(\phi)\ \Phi_{m_l}(\phi)\ d\phi = \delta_{m_l m'_l} \tag{11.18}$$

We can immediately note here that the function $\Phi_{m_l}(\phi)$ is an eigenfunction of the operator L_z with the eigenvalue $m_l\hbar$. Indeed,

$$\begin{aligned} L_z\ \Phi_{m_l}(\phi) &= -i\hbar \frac{\partial}{\partial\phi}\left(\frac{1}{\sqrt{2\pi}}\, e^{im_l\phi}\right) \\ &= m_l\hbar\left(\frac{1}{\sqrt{2\pi}}\, e^{im_l\phi}\right) \\ &= m_l\hbar\ \Phi_{m_l}(\phi) \end{aligned} \tag{11.19}$$

Let us now turn to Equation (11.16). Introducing the change of variable $\xi = \cos\theta$ and writing $\Theta(\theta) = P(\xi)$, the equation becomes

$$\frac{d}{d\xi}\left[(1-\xi^2)\,\frac{dP}{d\xi}\right] + \left(\lambda - \frac{m_l^2}{1-\xi^2}\right) P(\xi) = 0 \tag{11.20}$$

It is convenient to solve this equation in two steps—first for $m_l = 0$ and then for $m_l \neq 0$.

The Case $m_l = 0$

For $m_l = 0$, the above equation reduces to

$$(1 - \xi^2)\,\frac{d^2P}{d\xi^2} - 2\xi\,\frac{dP}{d\xi} + \lambda P = 0 \tag{11.21}$$

This is the well known *Legendre differential equation*. We attempt a power series solution of the form

$$P(\xi) = \sum_{k=0}^{\infty} a_k\ \xi^k \tag{11.22}$$

Substitution into (11.21) gives

$$\sum_{k=0}^{\infty} [(k+1)\ (k+2)\ a_{k+2} + \{\lambda - k(k+1)\}a_k]\ \xi^k = 0$$

This equation can be satisfied only if the coefficient of each power of ξ vanishes. This gives the *recurrence relation*

$$a_{k+2} = \frac{k\,(k+1) - \lambda}{(k+1)\,(k+2)}\, a_k \tag{11.23}$$

Since a_{k+2} is related to a_k, (11.22) may be written as

$$P(\xi) = a_0\left[1 + \frac{a_2}{a_0}\,\xi^2 + \frac{a_4}{a_0}\,\xi^4 + \ldots\right] + a_1\left[\xi + \frac{a_3}{a_1}\,\xi^3 + \frac{a_5}{a_1}\,\xi^5 + \ldots\right] \tag{11.24}$$

The two series inside the brackets represent the two linearly independent solutions of (11.21). Now, from (11.23) we note that

$$\lim_{k\to\infty} \frac{a_{k+2}}{a_k} = \lim_{k\to\infty} \frac{k}{k+2} = 1$$

Therefore, if the two series in (11.24) do not terminate at some value of k, they will diverge for $\xi = \pm 1$ (i.e., for $\theta = 0$ and π) and so will not be acceptable as a wave function.

From (11.23) we find that one of the two series will terminate if

$$\boxed{\lambda = l(l+1), \quad l = 0, 1, 2, \ldots} \tag{11.25}$$

For even values of l, the even series will terminate. The odd series can be made to vanish by choosing $a_1 = 0$. Similarly, for odd values of l, the odd series will terminate and the even series can be got rid of by choosing $a_0 = 0$.

The possible eigenvalues of the operator L^2 are seen to be

$$\boxed{\lambda\hbar^2 = l(l+1)\hbar^2 = 0, 2\hbar^2, 6\hbar^2, 12\hbar^2, \ldots} \tag{11.26}$$

as l assumes the values 0, 1, 2, 3, … . Justifiably, l is called the *orbital angular momentum quantum number*.

Legendre Polynomials

The physically acceptable solutions of the Legendre equation are thus polynomials. These are called the *Legendre polynomials*, denoted $P_l(\xi)$, where l is the degree of the polynomial. These polynomials are uniquely defined apart from an arbitrary multiplicative constant which, by convention, is chosen so that

$$P_l(1) = 1 \tag{11.27}$$

Also, since $P_l(\xi)$ contains only even or odd powers of ξ, depending on whether l is even or odd, we have

$$P_l(-\xi) = (-1)^l \, P_l(\xi) \tag{11.28}$$

The first few Legendre polynomials are:

$$\boxed{\begin{aligned} P_0(\xi) &= 1 \\ P_1(\xi) &= \xi \\ P_2(\xi) &= \frac{1}{2}(3\xi^2 - 1) \\ P_3(\xi) &= \frac{1}{2}(5\xi^3 - 3\xi) \\ P_4(\xi) &= \frac{1}{8}(35\xi^4 - 30\xi^2 + 3) \\ P_5(\xi) &= \frac{1}{8}(63\xi^5 - 70\xi^3 + 15\xi) \end{aligned}} \tag{11.29}$$

Below we give some important properties of the Legendre polynomials. The details can be found in any book on mathematical physics.

Rodrigues' Formula

$$P_l(\xi) = \frac{1}{2^l \cdot l!} \frac{d^l}{d\xi^l} (\xi^2 - 1)^l \tag{11.30}$$

Recurrence Relations

$$(l + 1) P_{l+1}(\xi) = (2l + 1)\xi P_l(\xi) - l P_{l-1}(\xi) \tag{11.31}$$

and

$$(1 - \xi^2) \frac{dP_l}{d\xi} = -l\xi P_l(\xi) + l P_{l-1}(\xi) \tag{11.32}$$

Generating Function

$$T(\xi, s) = (1 - 2\xi s + s^2)^{-1/2} = \sum_{l=0}^{\infty} P_l(\xi) s^l, \ |s| < 1 \tag{11.33}$$

Orthogonality

$$\int_{-1}^{+1} P_l(\xi) P_{l'}(\xi) d\xi = \frac{2}{2l+1} \delta_{ll'} \tag{11.34}$$

This equation shows that the Legendre polynomials are orthogonal over the range $-1 \le \xi \le 1$, but they are not normalized to unity.

The General Case $m_l \neq 0$

Without going into details, we mention that, in general, Equation (11.20) has physically acceptable solutions only if $\lambda = l(l + 1)$ and $|m_l| \le l$. These solutions are called *associated Legendre functions*. The associated Legendre function $P_l^{m_l}(\xi)$ of degree l and order m_l is defined in terms of the Legendre polynomial $P_l(\xi)$ as

$$\boxed{P_l^{m_l}(\xi) = (1 - \xi^2)^{m_l/2} \frac{d^{m_l}}{d\xi^{m_l}} P_l(\xi), \quad m_l = 0, 1, 2, \ldots, l} \tag{11.35}$$

This can be shown as follows:

Differentiating the Legendre equation for $P_l(\xi)$ [Equation (11.21)] after replacing λ by $l(l + 1)$, m_l times and then substituting (11.35) into it, we obtain the equation

$$\frac{d}{d\xi}\left[(1-\xi^2)\frac{dP_l^{m_l}}{d\xi}\right] + \left(l(l+1) - \frac{m_l^2}{1-\xi^2}\right) p_l^{m_l} = 0 \tag{11.36}$$

which is same as (11.20) with λ replaced by $l(l + 1)$.

Now, according to (11.17), m_l can have negative values also. However, Equation (11.36) remains unchanged if m_l is replaced by $-m_l$. Therefore, $P_l^{-m_l}$ must be equal to $P_l^{m_l}$, apart from a possible multiplicative constant.

Regarding the possible values of m_l, which is called the *magnetic quantum number* for reasons which will be clear later, it may be noted that since $P_l(\xi)$ is a polynomial of degree l, its $|m_l|$ th derivative, and hence $P_l^{m_l}(\xi)$, will vanish if $|m_l| > l$. Therefore, for a given l, there are only $(2l + 1)$ possible values of m_l:

$$\boxed{m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l} \tag{11.37}$$

Using (11.28) and (11.35) it can be shown that

$$P_l^{m_l}(-\xi) = (-1)^{l-m_l} P_l^{m_l}(\xi), \; m_l = 0, 1, 2, \ldots, l \tag{11.38}$$

The associated Legendre functions satisfy the **recurrence relations**

$$(2l + 1)\xi \; P_l^{m_l}(\xi) = (l - m_l + 1) \; P_{l+1}^{m_l}(\xi) + (l + m_l) \; P_{l-1}^{m_l}(\xi) \tag{11.39}$$

and

$$(2l + 1) \; (1 - \xi^2)^{1/2} \; P_l^{m_l - 1}(\xi) = P_{l+1}^{m_l}(\xi) - P_{l-1}^{m_l}(\xi) \tag{11.40}$$

and the **orthogonality relations**

$$\int_{-1}^{+1} P_l^{m_l}(\xi) \; P_{l'}^{m_l}(\xi) \; d\xi = \frac{2}{2l+1} \frac{(l+m_l)!}{(l-m_l)!} \delta_{ll'} \tag{11.41}$$

The first few associated Legendre functions are:

$$\boxed{\begin{aligned}
&P_1^1(\xi) = (1-\xi^2)^{1/2} \\
&P_2^1(\xi) = 3(1-\xi^2)^{1/2} \, \xi \\
&P_2^2(\xi) = 3(1-\xi^2) \\
&P_3^1(\xi) = \frac{3}{2}(1-\xi^2)^{1/2} \, (5\xi^2 - 1) \\
&P_3^2(\xi) = 15\xi(1-\xi^2) \\
&P_3^3(\xi) = 15(1-\xi^2)^{3/2}
\end{aligned}} \tag{11.42}$$

Coming back to the θ-equation (11.16), we may now assert that its physically admissible solutions $\Theta_{lm_l}(\theta)$, normalized so that

$$\int_0^\pi \Theta^*_{l'm_l}(\theta) \; \Theta_{lm_l}(\theta) \; \sin\theta \; d\theta = \delta_{ll'}$$

are given by

$$\left.\begin{aligned}
\Theta_{lm_l}(\theta) &= (-1)^{m_l} \left[\frac{(2l+1)(l-m_l)!}{2(l+m_l)!}\right]^{1/2} P_l^{m_l}(\cos\theta), \; m_l \geq 0 \\
&= (-1)^{m_l} \Theta_{l|m_l|}(\theta), \quad m_l < 0
\end{aligned}\right\} \tag{11.43}$$

The choice of the phase factor is in conformity with the one most commonly used in the literature.

11.5 SPHERICAL HARMONICS

Finally, using (11.14), (11.17) and (11.43) we obtain the common eigenfunctions of the operators L^2 and L_z as

$$Y_{lm_l}(\theta, \phi) = (-1)^{m_l} \left[\frac{(2l+1)\,(l-m_l)\,!}{4\pi\,(l+m_l)\,!} \right]^{1/2} P_l^{m_l}(\cos\theta)\, e^{im_l\phi},\ m_l \geq 0 \qquad (11.44)$$

and

$$Y_{lm_l}(\theta, \phi) = (-1)^{m_l}\, Y^*_{l,-m_l}(\theta, \phi), \qquad m_l \leq 0 \qquad (11.45)$$

These functions are known as the *spherical harmonics*. They satisfy the **orthonormality** condition

$$\begin{aligned} &\int Y^*_{l'm'_l}(\theta,\ \phi)\ Y_{lm_l}(\theta,\ \phi)\ d\Omega \\ &= \int_0^{2\pi} d\phi \int_0^{\pi} Y^*_{l'm'_l}(\theta,\ \phi)\ Y_{lm_l}(\theta,\ \phi)\ \sin\theta\ d\theta \\ &= \delta_{ll'}\ \delta_{m_l m'_l} \end{aligned} \qquad (11.46)$$

where the integration is over the full range of the angular variables (θ, ϕ) and $d\Omega$ is the element of solid angle: $d\Omega = \sin\theta\, d\theta\, d\phi$.

We have

$$L^2\, Y_{lm_l}(\theta, \phi) = l(l+1)\hbar^2\, Y_{lm_l}(\theta, \phi), \qquad l = 0, 1, 2, \ldots \qquad (11.47)$$

and

$$L_z\, Y_{lm_l}(\theta, \phi) = m_l \hbar\, Y_{lm_l}(\theta, \phi), \qquad |m_l| \leq l \qquad (11.48)$$

The first few spherical harmonics are given in Table 11.1.

Table 11.1 The First Few Spherical Harmonics

l	m_l	Spherical Harmonic $Y_{lm_l}(\theta,\ \phi)$
0	0	$Y_{0,0} = \dfrac{1}{(4\pi)^{1/2}}$
1	0	$Y_{1,0} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta$
	±1	$Y_{1,\pm1} = \mp\left(\dfrac{3}{8\pi}\right)^{1/2} \sin\theta\ e^{\pm i\phi}$
2	0	$Y_{2,0} = \left(\dfrac{5}{16\pi}\right)^{1/2} (3\ \cos^2\theta - 1)$
	±1	$Y_{2,\pm1} = \mp\left(\dfrac{15}{8\pi}\right)^{1/2} \sin\theta\ \cos\theta\ e^{\pm i\phi}$
	±2	$Y_{2,\pm2} = \left(\dfrac{15}{32\pi}\right)^{1/2} \sin^2\theta\ e^{\pm 2i\phi}$

(11.49)

Parity of Spherical Harmonics

Under the parity operation $\mathbf{r} \to -\mathbf{r}$, the spherical polar coordinates transform as

$$r \to -r,\ \theta \to \pi - \theta,\ \phi \to \phi + \pi$$

Thus, if P is the parity operator, then

$$\mathrm{P}[Y_{lm_l}(\theta,\ \phi)] = Y_{lm_l}(\pi - \theta,\ \phi + \pi)$$

Now,

$$P_l^{m_l}[\cos(\pi - \theta)] = P_l^{m_l}(-\cos\theta) = (-1)^{l-m_l}\ P_l^{m_l}(\cos\theta)$$

using (11.38). Also,

$$e^{im_l(\phi + \pi)} = e^{im_l\pi}\ e^{im_l\phi} = (-1)^{m_l}\ e^{im_l\phi}$$

Therefore,

$$P[Y_{lm_l}(\theta,\ \phi)] = (-1)^{l-m_l+m_l}\ Y_{lm_l} = (-1)^l\ Y_{lm_l} \qquad (11.50)$$

Thus Y_{lm_l} has the parity of l, that is, even parity for even l and odd parity for odd l.

11.6 EFFECT OF THE OPERATORS L_x AND L_y ON Y_{lm_l}

The effect of L_x and L_y on the function Y_{lm_l} can be conveniently studied by introducing the two operators

$$L_+ = L_x + i\ L_y \qquad (11.51a)$$

and

$$L_- = L_x - i\ L_y \qquad (11.51b)$$

These are called the *raising* and *lowering* operators respectively. The significance of these names will be clear shortly.

Using (11.9) these operators can be written in spherical polar coordinates as

$$L_+ = \hbar e^{i\phi}\left[\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right] \qquad (11.52a)$$

and

$$L_- = -\hbar e^{-i\phi}\left[\frac{\partial}{\partial\theta} - i\cot\frac{\partial}{\partial\phi}\right] \qquad (11.52b)$$

Now, we have

$$\frac{\partial}{\partial\phi}[Y_{lm_l}(\theta,\ \phi)] = im_l\ Y_{lm_l}(\theta,\ \phi)$$

To determine $\partial Y/\partial\theta$, we note that from (11.35) it can be shown that

$$\frac{dP_l^{m_l}}{d\xi} = \frac{1}{(1-\xi^2)^{1/2}}P_l^{m_l+1} - \frac{m_l\xi}{1-\xi^2}P_l^{m_l}$$

$$= -\frac{(l + m_l)\,(l - m_l + 1)}{(1 - \xi^2)^{1/2}} P_l^{m_l - 1} + \frac{m_l \xi}{1 - \xi^2} P_l^{m_l}$$

Now, using (11.44), we can derive the relations

$$L_+ Y_{lm_l}(\theta, \phi) = \hbar[l(l + 1) - m_l(m_l + 1)]^{1/2} Y_{l,m_l+1}(\theta, \phi) \quad (11.53a)$$

and

$$L_- Y_{lm_l}(\theta, \phi) = \hbar[l(l + 1) - m_l(m_l - 1)]^{1/2} Y_{l,m_l-1}(\theta, \phi) \quad (11.53b)$$

We note that the effect of L_+ on Y_{lm_l} is to generate a multiple of Y_{l,m_l+1}; the quantum number m_l increases by one unit. Similarly, the effect of L_- decreases the quantum number m_l by one unit. Hence the names raising and lowering operators. Now, from (11.51),

$$L_x = \frac{1}{2}(L_+ + L_-) \quad (11.54a)$$

and

$$L_y = \frac{1}{2i}(L_+ - L_-) \quad (11.54b)$$

Using (11.54) and (11.53), the result of the action of L_x and L_y on Y_{lm_l} can be immediately obtained.

Let us now find the expectation values of L_x and L_y in the state Y_{lm_l}. Using the above equations we find

$$\langle L_\pm \rangle = \int Y^*_{lm_l} L_\pm Y_{lm_l}\, d\Omega$$

$$= \hbar[l(l + 1) - m_l(m_l \pm 1)]^{1/2} \int Y_{lm_l} Y_{l,m_l \pm 1}\, d\Omega$$

$$= 0$$

by orthonormality of the spherical harmonics. It immediately follows that

$$\langle L_x \rangle = \langle L_y \rangle = 0 \quad (11.55)$$

However,

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \frac{1}{2}\langle L^2 - L_z^2 \rangle$$

$$= \frac{1}{2}[l(l + 1) - m_l^2]\hbar^2 \quad (11.56)$$

11.7 VECTOR MODEL OF ANGULAR MOMENTUM: SPACE QUANTIZATION

We can now summarize the behaviour of the quantum mechanical angular momentum as follows. We find that the *x*-and *y*-components of the angular momentum **L** are not zero, but their average values are always zero. Further, the maximum value of the component of **L** on the *z*-axis, which is $l\hbar$, is less than

the magnitude of **L**, which is $\sqrt{l(l+1)}\,\hbar$. These results can be conveniently visualized in terms of a model which is called the *vector model* of angular momentum.

According to this model, the orbital angular momentum vector **L** precesses about the *z*-axis such that its projection on the *z*-axis is constant. This property is frequently called *space quantization*. The magnitude of **L** is $\sqrt{l(l+1)}\,\hbar$ and its projection on the *z*-axis is quantized, the possible values of L_z being $m_l\hbar$, $m_l = -l, -l+1, \ldots, 0, l-1, l$, i.e., $(2l+1)$ values in all. Thus, the vector **L** lies on the surface of a cone of altitude $m_l\hbar$ with the *z*-axis as the axis of symmetry (Figure 11.2). The possible orientations of **L** for $l = 2$ are shown in Figure 11.3.

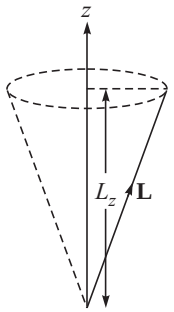


Figure 11.2 Precession of **L** about the *z*-axis.

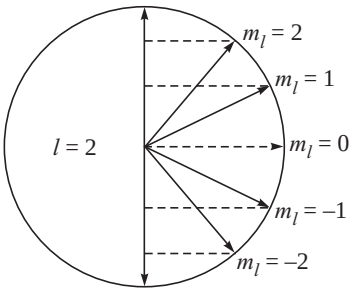


Figure 11.3 Possible orientations of **L** for $l = 2$.

This peculiar behaviour of the angular momentum in quantum mechanics is in accordance with the uncertainty principle. If **L** were fixed in space so that all the three components L_x, L_y and L_z had definite values, then the particle would have to be in a definite plane at all times. This would violate the uncertainty principle. For example, if **L** points permanently in the *z*-direction, the electron would be in the *xy* plane all the time. Since its *z*-coordinate gets fixed ($z = 0$), the *z*-component p_z of its momentum will have infinite uncertainty according to the uncertainty principle, which is impossible.

11.8 THE RIGID ROTATOR

Consider a particle of mass m, constrained to remain at a fixed distance R from a certain point, which we take as the origin of coordinates. The particle is otherwise free. In other words, the particle is free to move on the surface of a sphere whose centre is at the origin. This system is known as a *rigid rotator*. Its Hamiltonian is given by

$$H = \frac{L^2}{2I} \tag{11.57}$$

where $I = mR^2$ is the moment of inertia of the particle and L is its angular momentum. The Schrödinger equation can be written as

$$\frac{L^2}{2I}\psi(\theta,\phi) = E\psi(\theta,\phi)$$

or
$$L^2\psi(\theta,\phi) = 2IE\psi(\theta,\phi)$$

This is the eigenvalue equation for the operator L^2. We know that the eigenfunctions of L^2 are the spherical harmonics $Y_{lm_l}(\theta, \phi)$ and its eigenvalues are $l(l + 1)\hbar^2$, with $l = 0, 1, 2, \ldots$. Therefore, the *eigenfunctions of the rigid rotator are the spherical harmonics* $Y_{lm_l}(\theta, \phi)$ and the corresponding **energy eigenvalues** are

$$\boxed{E_l = \frac{\hbar^2}{2mR^2} l(l+1), \qquad l = 0, 1, 2, \ldots} \tag{11.58}$$

It may be noted that the energy eigenvalues do not depend on the quantum number m. So, the energy level E_l is $(2l + 1)$ fold *degenerate* because all the eigenfunctions $Y_{lm_l}(\theta, \phi)$ with $m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l$ correspond to the same energy. This degeneracy is a consequence of the fact that the Hamiltonian (11.57) commutes with the operator **L** and is therefore invariant under rotations. As such, all directions in space are equivalent and so the energy cannot depend on the orientation of the vector **L** with respect to an arbitrary axis, which is here the z-axis. Hence E must be independent of the quantum number m_l.

Equation (11.58) can be used to obtain the **rotational energy levels of a diatomic molecule**. In first approximation, a diatomic molecule can be considered as a rigid dumb-bell with the nuclei of the two atoms held at a fixed distance. Figure 11.4 shows the schematic diagram of a diatomic molecule, having nuclei A and B at distances R_A and R_B from their centre of mass. The axis of rotation (z-axis) is perpendicular to the line joining the two nuclei and passes through the centre of mass O. If m_A and m_B are the masses of the two nuclei, then the moment of inertia of the system is

$$I = m_A R_A^2 + m_B R_B^2 = mR^2$$

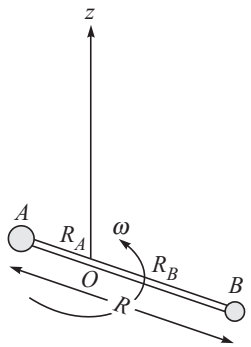


Figure 11.4 Rotation of a diatomic molecule.

where $m = m_A m_B/(m_A + m_B)$ is the reduced mass of the system and $R = R_A + R_B$ is the distance between the nuclei.

The Hamiltonian of the system is

$$H = \frac{L^2}{2I}$$

and the energy eigenvalues are given by (11.58).

SUMMARY

1. Orbital angular momentum is one of the fundamental constants of motion of an isolated three-dimensional system.
2. The orbital angular momentum operator in quantum mechanics is

$$\mathbf{L} = -i\hbar\,(\mathbf{r} \times \boldsymbol{\nabla})$$

It is most convenient to deal with the orbital angular momentum in spherical polar coordinates. The operators corresponding to L_x, L_y, L_z and L^2 in spherical coordinates are

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$L^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

3. These operators satisfy the following commutation relations:

$$[L_x,\ L_y] = i\hbar L_z$$
$$[L_y,\ L_z] = i\hbar L_x$$
$$[L_z,\ L_x] = i\hbar L_y$$
$$[L^2,\ L_x] = [L^2,\ L_y] = [L^2,\ L_z] = 0$$

These relations show that it is possible to find simultaneous eigenfunctions of L^2 and any one of L_x, L_y or L_z. Due to its simplest mathematical form L_z is chosen.

4. The eigenfunctions are found to be spherical harmonics given by

$$Y_{lm_l}(\theta,\ \phi) = (-1)^{m_l}\left[\frac{(2l+1)\,(l-m_l)\,!}{4\pi\,(l+m_l)\,!}\right]^{1/2} P_l^{m_l}(\cos\theta)\ e^{im_l\phi},\ m_l \geq 0$$

and $$Y_{lm_l}(\theta,\ \phi) = (-1)^{m_l}\ Y^*_{l,-m_l}(\theta,\ \phi), \quad m_l < 0$$

where $P_l^{m_l}(\cos\theta)$ are the associated Legendre functions. Y_{lm_l} has the parity of l.

5. It is found that

$$L^2\ Y_{lm_l}(\theta,\ \phi) = l(l+1)\hbar^2\ Y_{lm_l}(\theta,\ \phi),$$

and

$$L_z\ Y_{lm_l}(\theta,\ \phi) = m_l\hbar\ Y_{lm_l}(\theta,\ \phi),$$

$$l = 0,\ 1,\ 2,\ \ldots;$$

$$m_l = -l,\ -l+1,\ ..0,\ \ldots,\ l-1,\ l.$$

l is called the orbital angular momentum quantum number and m_l is called the magnetic quantum number.

6. Physically, the quantum mechanical angular momentum can be visualized in terms of the vector model. According to this model, the orbital angular momentum vector **L** precesses about the z-axis such that its projection on the z-axis is constant and is quantized. This property is called space quantization. The magnitude of **L** in state Y_{lm_l} is $\sqrt{l(l+1)}\,\hbar$ and the possible values of the projection L_z are the $(2l+1)$ values of $m_l\hbar$.

7. If a particle of mass m is constrained to move at a fixed distance R from the origin, its Hamiltonian is

$$H = \frac{L^2}{2mR^2}$$

Such a system, called a *rigid rotator,* obviously has the spherical harmonics Y_{lm_l} as the eigenfunctions and the corresponding energy eigenvalues are

$$E_l = \frac{\hbar^2}{2mR^2}\,l(l+1), \quad l = 0,\ 1,\ 2,\ \ldots$$

This equation can be used to obtain the rotational energy levels of a diatomic molecule if m is replaced by the reduced mass of the diatomic molecule.

QUESTIONS

1. Deduce the commutation relations for the components L_x, L_y, L_z of the orbital angular momentum operator and show that all the three commute with $L^2 = L_x^2 + L_y^2 + L_z^2$.
2. Express the angular momentum operators L_x, L_y, L_z and L^2 in spherical polar coordinates.
3. Obtain the eigenvalues and eigenfunctions of L^2 and L_z.
4. What are spherical harmonics? Show that these are common eigenfunctions of L^2 and L_z. Discuss the parity of spherical harmonics.
5. What are raising and lowering operators? Discuss their effect on the spherical harmonics. If L_+ is the raising operator and L_- is the lowering operator then show that

$$\langle L_\pm \rangle = 0$$

Using the result show that

$$\langle L_x \rangle = \langle L_y \rangle = 0$$

and $$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \frac{1}{2}[l(l+1) - m_l^2]\hbar^2$$

6. Discuss the vector model of angular momentum.
7. What is a rigid rotator? Write its Hamiltonian and obtain its eigenvalues and eigenfunctions.

Chapter

12 Spherically Symmetric Potentials and Hydrogenic Atoms

Chapter Contents

12.1 Separation of the Wave Equation into Radial and Angular Parts
12.2 Reduction of a Two-Body Problem to an Equivalent One-Body Problem
12.3 Hydrogenic Atoms
12.4 Effect of Magnetic Field on the Atomic Energy Levels: The Zeeman Effect

We shall now turn our attention to the study of the motion of a particle in a potential $V(r)$ which depends only on the magnitude r of the position vector $\mathbf{r}$ of the particle with respect to some origin. Such a potential is called a *spherically symmetric potential* or a *central potential*. This is one of the most important problems in quantum mechanics and forms the starting point of the application of quantum mechanics to the understanding of atomic and nuclear structure.

12.1 SEPARATION OF THE WAVE EQUATION INTO RADIAL AND ANGULAR PARTS

If m is the mass of the particle then its Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{12.1}$$

Since $V(r)$ is spherically symmetric, it is most convenient to use the spherical polar coordinates defined in chapter 11 [see Equation (11.8) and Figure 11.1]. Expressing the ∇^2 operator in spherical polar coordinates[†], the Hamiltonian (12.1) becomes

[†] This can be found in any standard textbook on mathematical physics.

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r) \tag{12.2}$$

Recalling from chapter 11 that the representation of the square of the angular momentum operator in spherical polar coordinates is given by (see Equation 11.10)

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{12.3}$$

We may write

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{L^2}{\hbar^2r^2}\right] + V(r) \tag{12.4}$$

The time-independent Schrödinger equation for the particle can be written as

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{12.5}$$

or
$$\left[-\frac{\hbar^2}{2m}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{L^2}{\hbar^2r^2}\right\}+V(r)\right]\psi(r,\ \theta,\ \phi) = E\psi(r,\ \theta,\ \phi)$$

or
$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{2m}{\hbar^2}[E - V(r)]\ \psi(r,\ \theta,\ \phi) = \frac{L^2}{\hbar^2r^2}\psi(r,\ \theta,\ \phi) \tag{12.6}$$

This equation can be solved by using the method of separation of variables. Let us write

$$\psi(r,\ \theta,\ \phi) = R(r)\ Y(\theta,\ \phi)$$

Substituting into (12.6),

$$\frac{Y(\theta,\phi)}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}[E - V(r)]\ R(r)Y(\theta,\ \phi) = \frac{R(r)}{\hbar^2r^2}\ L^2\ Y(\theta,\ \phi)$$

Dividing by $R(r)Y(\theta,\ \phi)/r^2$,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}[E - V(r)] = \frac{1}{\hbar^2Y}\ L^2Y(\theta,\ \phi) \tag{12.7}$$

The left-hand side of this equation depends only on r and the right-hand side depends only on θ and ϕ. Therefore, both sides must be equal to a constant. Calling this constant λ, we obtain the *radial equation*

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\{E - V(r)\} - \frac{\lambda}{r^2}\right] R(r) = 0 \tag{12.8}$$

and the *angular equation*

$$L^2Y(\theta,\ \phi) = \lambda\hbar^2Y(\theta,\ \phi) \tag{12.9}$$

The Angular Equation

Equation (12.9) is an eigenvalue equation for the operator L^2. We recall from section 11.4 that physically acceptable solutions of this equation are obtained for

$$\lambda = l(l + 1),\ l = 0,\ 1,\ 2,\ \ldots \tag{12.10}$$

Thus, the eigenvalues of L^2 are $l(l + 1)\hbar^2$, $l = 0, 1, 2, \ldots$. The corresponding eigenfunctions are the spherical harmonics $Y_{lm_l}(\theta, \phi)$ defined in Equations (11.44) and (11.45). The spherical harmonics $Y_{lm_l}(\theta, \phi)$ are also eigenfunctions of the z-component of the angular momentum L_z such that

$$L_z Y_{lm_l}(\theta, \phi) = m_l \hbar Y_{lm_l}(\theta, \phi),\ m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l \tag{12.11}$$

It may be noted that so long as the potential is spherically symmetric, whatever be its precise form, the angular eigenfunctions are always the spherical harmonics.

The Radial Equation

Substituting (12.10) into (12.8), the radial equation becomes

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right] R(r) = 0 \tag{12.12}$$

If we put

$$R(r) = u(r)/r$$

then the equation for the *new* radial function $u(r)$ is

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right] u(r) = 0 \tag{12.13}$$

This equation shows that the radial motion is similar to the one-dimensional motion of a particle in the "effective" potential

$$V_{\text{eff}} = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \tag{12.14}$$

The additional term $l(l + 1)\hbar^2/2mr^2$ is due to the "centrifugal barrier" which is a consequence of the non-zero angular momentum. This can be understood as follows: According to classical mechanics, if a particle has angular momentum L about an axis, then its angular velocity is

$$\omega = \frac{L}{mr^2}$$

where r is the distance of the particle from the axis. The "centrifugal force" on the particle is

$$mr\omega^2 = \frac{L^2}{mr^3}$$

The corresponding "centrifugal potential energy" of the particle is $L^2/2mr^2$. Putting $L^2 = l(l + 1)\hbar^2$ gives the additional term in (12.14). This term tends to infinity as $r \to 0$. Thus, it acts as a repulsive core and prevents the system from collapsing. Figure 12.1 shows typical shapes of the centrifugal barrier and the effective potential when the particle is moving under the Coulomb force.

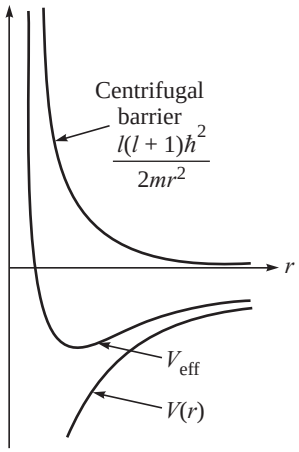


Figure 12.1 Shapes of the centrifugal barrier, effective potential and Coulomb potential.

In order to proceed further with the solution of the radial equation, we must know the precise form of the potential $V(r)$. In what follows we shall solve the radial equation for a hydrogenic atom, which consists of a nucleus and an electron interacting via the attractive Coulomb force which depends on the magnitude of the distance between the two. In the next section, we shall show that for a two-body system, if the potential energy depends only on the coordinates of one particle relative to the other, then the problem can be reduced to an equivalent one-body problem along with a uniform translational motion of the centre of mass of the two-body system. In section 12.3 we shall solve the equivalent one-body radial equation for a hydrogenic atom.

12.2 REDUCTION OF A TWO-BODY PROBLEM TO AN EQUIVALENT ONE-BODY PROBLEM

Consider two particles, of masses m_1 and m_2, interacting via a potential $V(\mathbf{r}_1 - \mathbf{r}_2)$ which depends only upon the relative coordinate $\mathbf{r}_1 - \mathbf{r}_2$. The time-independent Schrödinger equation for the system is

$$\left[-\frac{\hbar^2}{2m_1}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m_2}\nabla^2_{\mathbf{r}_2} + V(\mathbf{r}_1 - \mathbf{r}_2)\right]\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\ \Psi(\mathbf{r}_1, \mathbf{r}_2) \qquad (12.15)$$

where E is the total energy of the system. Let us now introduce the *relative coordinate*

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{12.16}$$

and the *centre-of-mass coordinate*

$$R = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \tag{12.17}$$

A simple calculation will show that

$$-\frac{\hbar^2}{2m_1}\nabla^2_{\mathbf{r}_1} - \frac{\hbar^2}{2m_2}\nabla^2_{\mathbf{r}_2} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} \tag{12.18}$$

where

$$M = m_1 + m_2 \tag{12.19}$$

and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{12.20}$$

The quantity μ is called the *reduced* mass of the two-particle system. The Schrödinger Equation (12.15) becomes

$$\left[-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\Psi(\mathbf{R}, \mathbf{r}) = E\ \Psi(\mathbf{R}, \mathbf{r}) \tag{12.21}$$

Now, since the potential $V(\mathbf{r})$ depends only on the relative coordinate, the wave function $\Psi(\mathbf{R}, \mathbf{r})$ can be written as a product of functions of $\mathbf{R}$ and $\mathbf{r}$:

$$\Psi(\mathbf{R}, \mathbf{r}) = \Phi(\mathbf{R})\ \psi(\mathbf{r}) \tag{12.22}$$

Substituting into (12.21) it can be easily shown that the functions $\Phi(\mathbf{R})$ and $\psi(\mathbf{r})$ satisfy, respectively, the equations

$$-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\Phi(\mathbf{R}) = E_{\mathbf{R}}\Phi(\mathbf{R}) \tag{12.23}$$

and

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}} + V(\mathbf{r})\right]\psi(\mathbf{r}) = E_{\mathbf{r}}\psi(\mathbf{r}) \tag{12.24}$$

Equation (12.23) describes the motion of the centre of mass. It says that the centre of mass moves as a free particle of mass M and energy E_R. Equation (12.24) describes the relative motion of the particles. It says that the relative motion is same as that of a particle of mass μ moving in the potential $V(\mathbf{r})$. Clearly

$$E = E_R + E_r \tag{12.25}$$

In a physical problem, we are mainly interested in the eigenvalues and eigenvectors connected with the relative motion. Therefore, we shall be concerned only with the solution of Equation (12.24). Thus, by separating the centre-of-mass motion, the solution of the problem gets considerably simplified.

12.3 HYDROGENIC ATOMS

Let us consider a one-electron atom having atomic number Z. We know that $Z = 1$ for the hydrogen atom (H), $Z = 2$ for the singly ionized helium atom (He^+), $Z = 3$ for the doubly ionized lithium atom (L_i^{++}), and so on. Such atoms are called hydrogenic atoms or hydrogen-like atoms. The charge on the nucleus is Ze and that on the electron is $-e$. The potential energy due to the attractive Coulomb interaction between them is

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{12.26}$$

which depends only on the distance r between the nucleus and the electron and hence is spherically symmetric.

If m is the mass of the electron and M is the mass of the nucleus, then the reduced mass of the system is

$$\mu = \frac{mM}{m+M} \tag{12.27}$$

Since the nuclear mass M is much larger than the electron mass m, the reduced mass μ is very close to m. Therefore, henceforth we shall replace μ by m. That is, we shall consider the nucleus to be stationary. The correction for the nuclear mass is then simply a matter of replacing m by μ.

The radial Equation (12.12) becomes

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2}\right]R(r) = 0 \tag{12.28}$$

Since we are interested only in the energies associated with the relative motion, we may assume that we are working in the centre-of-mass system, so that $E_R = 0$ and the total energy E is equal to the energy E_r of relative motion. Further, we shall be interested only in the bound state solutions and therefore, we shall consider $E < 0$.

In order to solve (12.28), it is convenient to introduce the dimensionless variable ρ and the dimensionless constant λ defined by

$$\rho = \left(-\frac{8mE}{\hbar^2}\right)^{1/2} r \tag{12.29}$$

and

$$\lambda = \frac{Ze^2}{4\pi\varepsilon_0\hbar}\left(\frac{-m}{2E}\right)^{1/2} = Z\alpha\left(\frac{-mc^2}{2E}\right)^{1/2} \tag{12.30}$$

where $\alpha = e^2/(4\pi\varepsilon_0\hbar c) \approx 1/137$ is the well known fine-structure constant. In terms of ρ and λ, Equation (12.28) becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0 \tag{12.31}$$

In order to solve this equation, we first examine the asymptotic behaviour of $R(\rho)$. We note that as $\rho \to \infty$, Equation (12.31) reduces to

$$\frac{d^2R}{d\rho^2} - \frac{1}{4}R(\rho) = 0 \tag{12.32}$$

The solutions of this equation are proportional to exp $(\pm\rho/2)$. Out of these only exp $(-\rho/2)$ is acceptable because exp $(\rho/2)$ becomes unbounded as $\rho \to \infty$. This suggests that the exact solution of (12.31) must be of the form

$$R(\rho) = e^{-\rho/2}F(\rho) \tag{12.33}$$

Substitution into (12.31) gives the equation for $F(\rho)$ as

$$\rho^2 \frac{d^2F}{d\rho^2} + \rho(2 - \rho)\frac{dF}{d\rho} + [(\lambda - 1)\rho - l(l + 1)]F(\rho) = 0 \tag{12.34}$$

When $\rho = 0$, this equation yields

$$l(l + 1)F(0) = 0$$

or
$$F(0) = 0 \quad \text{for} \quad l \neq 0 \tag{12.35}$$

This shows that a power series solution for $F(\rho)$ cannot contain a constant term. Therefore, we try a series solution of the form

$$F(\rho) = \sum_{k=0}^{\infty} a_k \rho^{s+k} \tag{12.36}$$

Substituting into (12.34) and simplifying, we obtain

$$\sum_{k=0}^{\infty} a_k[(s + k)(s + k + 1) - l(l + 1)]\rho^k - \sum_{k=0}^{\infty} a_k[s + k + 1 - \lambda]\rho^{k+1} = 0 \tag{12.37}$$

For this equation to be valid, the coefficient of each power of ρ must vanish. Equating the coefficient of ρ^0 to zero gives

$$s(s + 1) - l(l + 1) = 0$$

or
$$(s - l)(s + l + 1) = 0$$

Thus,
$$s = l \quad \text{or} \quad s = -(l + 1) \tag{12.38}$$

If we take $s = -(l + 1)$, then the first term in the expansion (12.36) would be a_0/ρ^{l+1}, which tends to infinity as $\rho \to 0$. Therefore, the acceptable value is $s = l$. Now, setting the coefficient of ρ^{k+1} in (12.37) equal to zero, we obtain

$$a_{k+1}[(s + k + 1)(s + k + 2) - l(l + 1)] - a_k(s + k + 1 - \lambda) = 0$$

Putting $s = l$ and rearranging, we obtain the *recurrence relation*

$$a_{k+1} = \frac{k + l + 1 - \lambda}{(k + 1)(k + 2l + 2)} a_k \tag{12.39}$$

This relation determines the coefficients a_1, a_2, a_3,… in terms of a_0 which can be arbitrary. In order to infer the behaviour of the series (12.36) for large values of k, we note that

$$\lim_{k\to\infty} \frac{a_{k+1}}{a_k} = \frac{1}{k}$$

This is similar to the asymptotic behaviour of the expansion of the function exp (ρ) as shown below. We have

$$e^{\rho} = \sum_{k=0}^{\infty} c_k \rho^k$$

where

$$c_k = \frac{1}{k!}$$

Therefore,

$$\frac{c_{k+1}}{c_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1}$$

So,

$$\lim_{k\to\infty} \frac{c_{k+1}}{c_k} = \frac{1}{k}$$

Thus, if the series (12.36) does not terminate, then $F(\rho)$ will behave as exp (ρ) and so, according to (12.33), $R(\rho)$ will behave as exp (ρ/2), which diverges as $\rho \to \infty$. Since this is not acceptable, the series must terminate at some value of k, say n_r. This can be possible if we require that λ be equal to a positive integer n such that

$$\boxed{\lambda = n = n_r + l + 1} \tag{12.40}$$

In that case a_{k+1}, and hence all higher coefficients, will be zero. Since both n_r and l can be positive integers or zero, it is clear that n can have only positive integral values. n_r is called the *radial quantum number* and n the *principal quantum number*. Note that for a given n the allowed values of l are 1, 2, …, n – 1.

Energy Eigenvalues

Equations (12.30) and (12.40) give the bound-state energy eigenvalues

$$\boxed{\begin{aligned} E_n &= -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} \\ &= -\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}, \qquad n = 1, 2, 3, \ldots \end{aligned}} \tag{12.41}$$

This formula agrees exactly with the one obtained from the Bohr model (see Equation 3.17, section 3.3.), which was based on ad-hoc assumptions.

It was the most important early success of Schrödinger's theory because it could reproduce Bohr's formula from a general equation of motion. As discussed in chapter 3, the calculations based on this formula explain the main features of the experimental spectrum of hydrogen. However, the agreement is not perfect and various corrections, especially for the fine structure arising from the relativistic effects and the electron spin, must be taken into account to obtain detailed agreement with the experiment.

It may be noted that n may take all integral values from 1 to ∞. As such, the bound-state energy spectrum of a system held by the Coulomb force contains an *infinite* number of discrete energy levels. This is because the magnitude of the Coulomb potential decreases slowly at larger r. On the other hand, short-range forces have a finite number of bound states.

Degeneracy

Another very important point to note is that the energy eigenvalues depend only the principal quantum number n. There is no dependence on l and m_l. On the other hand, the eigenfunctions for a hydrogenic atom are determined by the values of three quantum numbers n, l and m_l. So for each energy level E_n given by (12.41) there are more than one distinct state which have the same energy. This phenomenon is called **degeneracy**. The Bohr model was extremely inadequate because it did not account for degeneracy, which has important consequences as we shall see later.

The degeneracy with respect to the quantum number m_l is present for all spherically symmetric potentials. The degeneracy with respect to the quantum number l is characteristic of the $1/r$ Coulomb potential—it is removed if the potential function is even slightly modified. This happens in atoms more complex than hydrogen.

Let us find the total degeneracy of the energy level E_n. For a given value of n, the quantum number l may take any of the values 0, 1, …, $n - 1$. For each value of l, the quantum number m_l may take any of the $(2l + 1)$ possible values $-l, -l + 1, \ldots, 0, \ldots, l - 1, l$. The total degeneracy of the level is therefore given by

$$\sum_{l=0}^{n} (2l + 1) = 2\frac{n(n-1)}{2} + n = n^2 \qquad (12.42)$$

It is important to mention here that there is yet another property that increases the degeneracy further. Electrons (also protons and neutrons) have an intrinsic angular momentum called *spin*, that makes them fall in two possible states but the energy of the hydrogen atom is independent of these states. As a result, the degeneracy of the atom is $2n^2$, not n^2. We shall discuss spin in detail in the next chapter.

Figure 12.2 shows schematically the energy levels of hydrogen atom. The degenerate energy levels with the same n but different l are shown separately.

These levels are labelled by two symbols according to the standard **spectroscopic notation**. The first is a number which represents the principal quantum number n; the second is a letter which indicates the value of the orbital angular momentum quantum number l according to the following scheme:

Value of l	0	1	2	3	4	5...
Letter	*s*	*p*	*d*	*f*	*g*	*h*...

and so on alphabetically. The choice of the letters *s*, *p*, *d* and *f* originated during the initial period of the development of spectroscopy and has no physical significance.

According to this notation, the ground state ($n = 1$, $l = 0$) is a 1*s* state, the first excited state ($n = 2$, $l = 0, 1$) is four-fold degenerate, having one 2*s* state and three 2*p* states with $m_l = -1, 0, +1$, and so on, as shown in the figure. All the m_l-states corresponding to a particular value of l are drawn slightly apart to show their multiplicity, but they are degenerate.

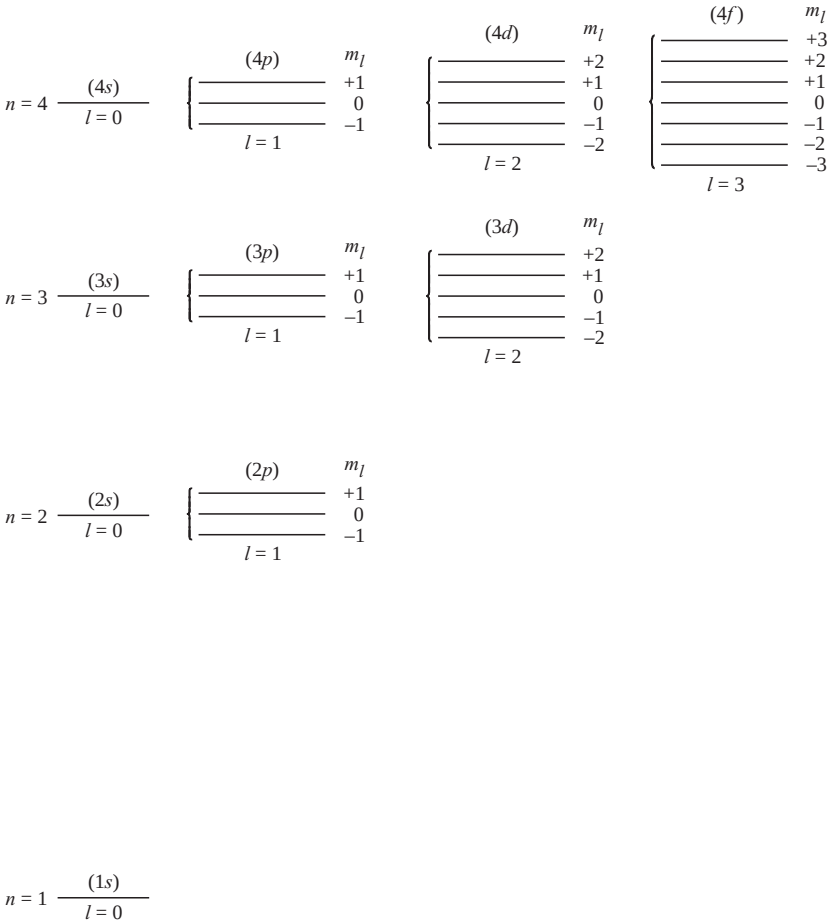


Figure 12.2 Schematic energy level diagram of hydrogen atom. The spacing between the non-degenerate levels is not to scale.

Radial Eigenfunctions

Let us now come back to the solution of (12.34). The above discussion suggests that we seek a solution of the form

$$F(\rho) = \rho^l L(\rho) \tag{12.43}$$

where $L(\rho)$ is a polynomial. Substituting in (12.34) and putting $\lambda = n$ gives the differential equation satisfied by $L(\rho)$ as

$$\rho \frac{d^2L}{d\rho^2} + (2l + 2 - \rho)\frac{dL}{d\rho} + (n - l - 1)\, L(\rho) = 0 \tag{12.44}$$

The physically acceptable solutions of this equation may be expressed in terms of *associated Laguerre polynomials*. To see this we first define the *Laguerre polynomials* $L_q(\rho)$ in terms of a generating function $U(\rho, s)$:

$$U(\rho, s) = \frac{\exp[-\rho s/(1-s)]}{1-s} = \sum_{q=0}^{\infty} \frac{L_q(\rho)}{q!} s^q, \; |s|<| \tag{12.45}$$

Differentiating in turn with respect to s and ρ yields the recurrence formulae

$$L_{q+1}(\rho) - (\rho - 1 - 2q)\, L_q(\rho) + q^2\, L_{q-1}(\rho) = 0 \tag{12.46}$$

and

$$\frac{d}{d\rho} L_q(\rho) - q \frac{d}{d\rho} L_{q-1}(\rho) + q\, L_{q-1}(\rho) = 0 \tag{12.47}$$

It can be easily seen that the lowest order differential equation involving only $L_q(\rho)$ that can be constructed from (12.46) and (12.47) is

$$\rho \frac{d^2}{d\rho^2} L_q + (1 - \rho)\frac{dL_q}{d\rho} + qL_q(\rho) = 0 \tag{12.48}$$

We now define the *associated Laguerre polynomial* as

$$L_q^p(\rho) = \frac{d^p}{d\rho^p} L_q(\rho) \tag{12.49}$$

Differentiating (12.48) p times, we can show that $L_q^p(\rho)$ satisfies the differential equation

$$\rho \frac{d^2 L_q^p}{d\rho^2} + (p + 1 - \rho)\frac{dL_q^p}{d\rho} + (q - p)L_q^p(\rho) = 0 \tag{12.50}$$

Comparing (12.50) with (12.44) we see that the physically acceptable solutions of (12.44) are the associated Laguerre polynomials $L_{n+l}^{2l+1}(\rho)$. Note that the order of L_{n+l}^{2l+1} is $(n + l) - (2l + 1) = n - l - 1 = n_r$, as required (see Equation 12.40).

The generating function for the associated Laguerre polynomials can be obtained by differentiating (12.45) p times with respect to ρ:

$$U_p(\rho, s) = \frac{(-1)^p \exp[-\rho s/(1-s)]}{(1-s)^{p+1}}$$

$$= \sum_{q=p}^{\infty} \frac{L_q^p(\rho)}{q!} s^q, \ |s|<1 \qquad (12.51)$$

The explicit expression for $L_{n+l}^{2l+1}(\rho)$ is found to be

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-l-1-k)!\,(2l+1+k)!} \frac{\rho^k}{k!} \qquad (12.52)$$

This can be verified by substituting into (12.51) with $q = n + l$ and $p = 2l + 1$.

Combining (12.33) and (12.43) we may write the full radial eigenfunction as

$$R_{nl}(r) = Ne^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \qquad (12.53)$$

where N is the normalization constant and

$$\rho = \left(\frac{-8mE_n}{\hbar^2}\right)^{1/2} r = \left(\frac{2Zme^2}{n(4\pi\varepsilon_0)\hbar^2}\right) r = \left(\frac{2Z}{na_0}\right) r \qquad (12.54)$$

a_0 being the radius of the first Bohr orbit for hydrogen:

$$a_0 = (4\pi\varepsilon_0)\hbar^2/me^2$$

The constant N is determined by requiring that

$$\int_0^{\infty} |R_{nl}(r)|^2 r^2 \, dr = 1$$

or

$$N^2\left(\frac{na_0}{2Z}\right)^3 \int_0^{\infty} e^{-\rho} \rho^{2l} [L_{n+l}^{2l+1}(\rho)]^2 \rho^2 d\rho = 1$$

The integral can be evaluated by using the generating function (12.51). It is found that the value of the integral is

$$\frac{2n[(n+l)!]^3}{(n-l-1)!}$$

This gives

$$\boxed{R_{nl}(r) = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho)} \qquad (12.55)$$

The **complete normalized energy eigenfunctions** for the hydrogenic atoms are, therefore,

$$\boxed{\begin{aligned} &\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)\, Y_{lm_l}(\theta, \phi) \\ &n = 1, 2, 3, \ldots; \quad l = 0, 1, 2, \ldots, n-1 \\ &m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \end{aligned}} \qquad (12.56)$$

The first three radial eigenfunctions are:

$$\boxed{\begin{aligned} R_{10} &= 2\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right) \\ R_{20} &= \left(\frac{Z}{2a_0}\right)^{3/2} \left(2-\frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right) \\ R_{21} &= \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right) \end{aligned}} \tag{12.57}$$

Figure 12.3 shows the graph of these three radial functions. It may be noted that only for the *s*-states ($l = 0$) are the radial functions different from zero at $r = 0$. This is due to the presence of the factor r^l in the expression for R_{nl}.

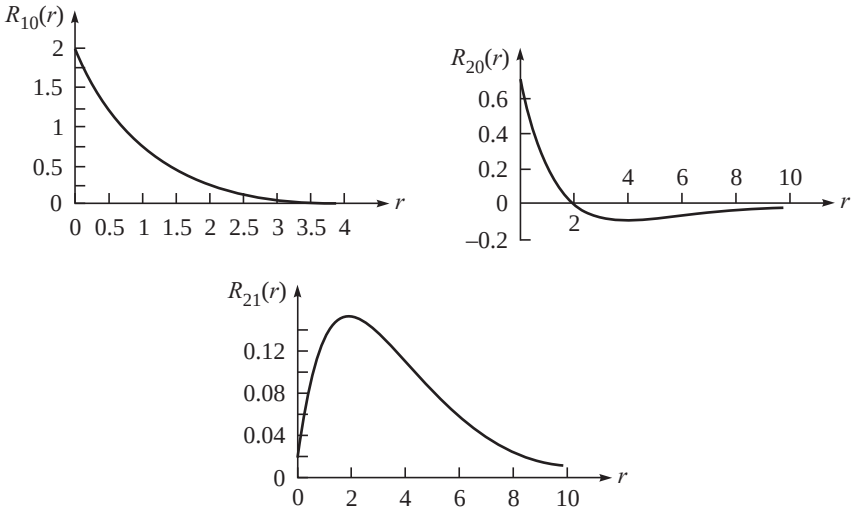


Figure 12.3 Radial functions $R_{10}(r)$, $R_{20}(r)$ and $R_{21}(r)$ for hydrogen atom. The unit of length is a_0.

The complete eigenfunctions for the lowest few states are:

$$\left.\begin{aligned} \psi_{100} &= \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right) \\ \psi_{200} &= \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(1-\frac{Zr}{2a_0}\right) \exp\left(\frac{-Zr}{2a_0}\right) \\ \psi_{210} &= \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a_0}\right)^{5/2} r \exp\left(\frac{-Zr}{2a_0}\right) \cos\theta \\ \psi_{21\pm1} &= \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} r \exp\left(\frac{-Zr}{2a_0}\right) (\sin\theta)\, e^{\pm i\phi} \end{aligned}\right\} \tag{12.58}$$

PROBLEM 12.1 Obtain the average distance of the electron from the nucleus for the ground state of a hydrogenic atom.

Solution: If a state is described by the wave function $\psi_{nlm_l}(r, \theta, \phi)$, then the expectation value of any function of position, $f(r, \theta, \phi)$, is

$$\langle f(r, \theta, \phi)\rangle = \int \psi^*_{nlm_l} f(r, \theta, \phi)\ \psi^*_{nlm_l}\, d\mathbf{r}$$

where
$$d\mathbf{r} = r^2\, dr\, \sin\theta\, d\theta\, d\phi$$

Here

$$f(r, \theta, \phi) = r$$
$$\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)\ Y_{lm_l}(\theta, \phi)$$

Thus,

$$\langle r\rangle = \int_0^\infty |R_{nl}|^2\ r^3\ dr \left[\int_0^{2\pi}\int_0^{\pi} |Y_{lm_l}(\theta, \phi)|^2 \sin\theta\, d\theta\, d\phi\right]$$

Since the spherical harmonics Y_{lm_l} are normalized, the value of the angular integral is unity.

This shows that for finding the expectation value of a quantity which depends only on r, we need consider only the radial function $R_{nl}(r)$.

For the ground state, $n = 1$, $l = 0$. So,

$$\langle r\rangle = \int_0^\infty |R_{10}(r)|^2\ r^3\ dr$$

Now,

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(\frac{-Zr}{a_0}\right)$$

Therefore,

$$\langle r\rangle = \frac{4Z^3}{a_0^3}\int_0^\infty \exp\left(\frac{-2Zr}{a_0}\right) r^3\, dr$$

Using the standard integral

$$\int_0^\infty r^n\, e^{-ar} dr = \frac{n!}{a^{n+1}},$$

we obtain

$$\langle r\rangle = \boxed{\frac{3a_0}{2Z}}$$

Note that larger the value of Z, smaller is the value of $\langle r\rangle$. This is expected because higher the charge on the nucleus, more is the inward pull on the electron.

PROBLEM 12.2 Calculate the most probable distance of the electron in the ground state of a hydrogenic atom. What is the radial probability density at that distance?

Solution: Radial probability density

$$P_{nl}(r) = r^2 \, |R_{nl}(r)|^2$$

For the ground state

$$P_{10}(r) = \left| 2\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(\frac{-Zr}{a_0}\right) \right|^2 r^2$$

$$= \frac{4Z^3}{a_0^3} r^2 \exp\left(\frac{-2Zr}{a_0}\right)$$

$P_{10}(r)$ will be maximum when

$$\frac{dP_{10}}{dr} = 0$$

or $$\left(\frac{-2Z}{a_0}\right) r^2 \exp\left(\frac{-2Zr}{a_0}\right) + 2r \exp\left(\frac{-2Zr}{a_0}\right) = 0$$

or $$r = \boxed{\frac{a_0}{Z}}$$

This is the required most probable distance. The maximum value of the radial probability density is

$$(P_{10})_{\max} = \frac{4Z^3}{a_0^3}\left(\frac{a_0}{Z}\right)^2 \exp\left(\frac{-2Z}{a_0}\frac{a_0}{Z}\right)$$

$$= \boxed{\frac{4Z}{a_0} e^{-2}}$$

PROBLEM 12.3 Calculate $\langle 1/r \rangle$ for an electron in the ground state of a hydrogenic atom and use the result to calculate (a) the average potential energy and (b) the average kinetic energy.

Solution:

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty |R_{10}(r)|^2 \, \frac{1}{r} \, r^2 dr$$

$$= \frac{4Z^3}{a_0^3} \int_0^\infty r \exp\left(\frac{-2Zr}{a_0}\right) dr = \frac{Z}{a_0}$$

(a) Average potential energy $\langle V(r) \rangle = \left\langle \frac{-Ze^2}{4\pi\varepsilon_0 r} \right\rangle = -\frac{Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle$

$$= -\frac{Z^2 e^2}{4\pi\varepsilon_0 a_0}$$

$$= -\frac{Z^2 e^2}{4\pi\varepsilon_0}\left(\frac{me^2}{4\pi\varepsilon_0 \hbar^2}\right)$$

$$= -\frac{m}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 = -mc^2\, Z^2\alpha^2$$

(b) Average kinetic energy

$$\langle K\rangle = E - \langle V(r)\rangle$$

$$= -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 - \left[\frac{-m}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\right]$$

$$= \frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 = \frac{mc^2\, Z^2\alpha^2}{2}$$

We note that

$$\langle K\rangle = -\frac{1}{2}\langle V(r)\rangle$$

This result is the quantum mechanical equivalent of the classical "virial theorem". It is true not only for the ground state, but for all bound states of hydrogenic atoms.

PROBLEM 12.4 The ground-state wave function for hydrogen is

$$\psi(r) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

Calculate the probability of finding the electron at a distance (a) less than a_0 from the nucleus, (b) between $a_0/2$ and $2a_0$ from the nucleus.

Solution: (a) Required probability $P_1 = \int_0^{a_0} |\psi(r)|^2\, 4\pi\, r^2 dr$

The factor 4π is the value of the integral over the angular variables:

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta = 4\pi$$

Thus

$$P_1 = \frac{4}{a_0^3}\int_0^{a_0} r^2\, e^{-2r/a_0} dr$$

We know from the table of indefinite integrals

$$\int r^2\, e^{-2r/a_0} dr = \left(-\frac{a_0 r^2}{2} - \frac{a_0^2 r}{2} - \frac{a_0^3}{4}\right) e^{-2r/a_0}$$

Taking the limits from 0 to a_0,

$$\int_0^{a_0} r^2\, e^{-2r/a_0} dr = \left[\frac{-5a_0^3 e^{-2}}{4} + \frac{a_0^3}{4}\right] = \frac{a_0^3}{4}(1 - 5e^{-2})$$

Hence $$P_1 = 1 - 5e^{-2} = \boxed{0.323}$$

(b) Required probability $$P_2 = \frac{4}{a_0^3}\int_{a_0/2}^{2a_0} r^2\, e^{-2r/a_0}\, dr$$

$$= \frac{5}{2}e^{-1} - 13e^{-4}$$

$$= \boxed{0.682}$$

12.4 EFFECT OF MAGNETIC FIELD ON THE ATOMIC ENERGY LEVELS: THE ZEEMAN EFFECT

The **Zeeman effect** is the *splitting of atomic energy levels and, consequently, the associated spectral lines when the atoms are placed in a magnetic field.* This effect provides a strong experimental confirmation of the quantization of angular momentum and also tells why m_l is called the magnetic quantum number. Michael Faraday had suggested, towards the middle of the nineteenth century, that the spectrum of a light source would change if it is placed in a strong magnetic field. However, he was unable to observe any effect because the spectroscopes of his days did not have sufficient resolving power. In 1896, Peter Zeeman repeated the experiment with equipment of high resolving power. He found that many spectral lines were split into groups of closely spaced lines. H.A. Lorentz developed a theory to explain this effect. Zeeman and Lorentz were jointly awarded the 1902 Nobel Prize in physics.

Lorentz's explanation of the splitting of lines was based on classical physics. We shall not discuss it. According to this theory, a spectral line must split into *three* components—one of these has the same frequency as the original line and the other two have frequencies higher and lower than the original frequency by the same amount. This is indeed observed in the spectra of some elements under certain conditions and is called the **normal Zeeman effect.** However, in most of the cases a line is split into more than three components and even when only three components are present, there spacing does not always agree with the prediction of the classical theory. Due to this reason it was called the **anomalous Zeeman effect.** The name still persists even though there is nothing "anomalous" about it now.

A complete understanding of the Zeeman effect could be possible quantum mechanically only after the concept of electron spin was introduced by Goudsmidt and Uhlenbeck in 1925. In fact, explanation of anomalous Zeeman effect was one of the reasons for the introduction of electron spin. However, the normal Zeeman effect can be explained if we ignore spin and consider only the orbital motion of the electron. We shall do so in this section. We must first understand how an orbiting electron has properties that cause it to be affected by a magnetic field.

Magnetic Moment of an Orbiting Electron

An orbiting electron is equivalent to a current loop and, therefore, it behaves as a magnetic dipole. The magnetic moment of a current loop is given by

$$\boldsymbol{\mu} = I\mathbf{A} \tag{12.59}$$

where I is the current flowing through the loop and **A** is the vector area enclosed by the loop. The direction of **A** is perpendicular to the loop and is given by the usual right-hand rule. The current I is the rate at which charge flows past a point and so is equal to e/T, where T is the time period of revolution and e is the electronic charge. If v is the speed of the electron and r is the radius of the orbit, then $T = 2\pi r/v$ and $A = \pi r^2$. Thus, the magnetic moment has the magnitude

$$\mu = \frac{ev}{2\pi r}\pi r^2 = \frac{1}{2}\, evr$$

We can express this in terms of the magnitude of the angular momentum which is $L = mvr$. We obtain

$$\mu = \frac{e}{2m}L \tag{12.60}$$

Since the direction of vector **L** is same as the direction of vector **A** and the charge on the electron is negative, the direction of $\boldsymbol{\mu}$ is opposite to that of **L**. Thus, in vector notation

$$\boxed{\boldsymbol{\mu} = -\left(\frac{e}{2m}\right)\mathbf{L} \quad \textbf{(Orbital magnetic moment of electron)}} \tag{12.61}$$

The ratio of the magnitude of $\boldsymbol{\mu}$ to that of **L** is

$$\boxed{\frac{\mu}{L} = \frac{e}{2m}} \tag{12.62}$$

and is called the *gyromagnetic ratio.*

Expression (12.61) has been obtained using classical physics. However, it remains true in quantum mechanics. Though the concept of orbit is not valid in quantum mechanics, a quantum state does indeed have an angular momentum.

According to Bohr's theory, $L = n\hbar$, where $n = 1, 2, 3, \ldots$. For the ground state, $n = 1$ and so (12.60) becomes $\mu = (e/2m)\hbar$. Though Bohr's theory is not correct, this quantity serves as a convenient unit for magnetic moment. It is called the **Bohr magneton,** denoted by μ_B:

$$\boxed{\mu_B = \frac{e\hbar}{2m} \quad \textbf{(Bohr magneton)}} \tag{12.63}$$

Its numerical value is

$$\mu_B = 9.274 \times 10^{-24}\ \text{J/T or A·m}^2$$

Effect of External Magnetic Field: Splitting of Energy Levels

It is well known that when a magnetic dipole of moment $\boldsymbol{\mu}$ is placed in a magnetic field **B**, it experiences a torque $\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B}$. The potential energy of the dipole in the field is given by

$$U = -\boldsymbol{\mu}\cdot\mathbf{B} \tag{12.64}$$

Now, suppose a hydrogen atom is placed in a magnetic field **B**. Since the electron in an orbit acts as a magnetic dipole of dipole moment given by (12.61), its potential energy in the field would be

$$U = \left(\frac{e}{2m}\right)\mathbf{B}\cdot\mathbf{L} \tag{12.65}$$

Let the magnetic field be directed along the z-axis. Then

$$U = \frac{e}{2m}BL_z \tag{12.66}$$

This potential energy must be substituted into the Schrödinger equation alongside the potential energy due to the Coulomb force. However, we know that the angular part of the wave function, $Y_{lm_l}(\theta, \phi)$, is an eigenfunction of the operator L_z with eigenvalue $m_l\hbar$. Therefore, the energy of the electron in the magnetic field is

$$E' = E_n + \frac{e\hbar}{2m}Bm_l$$
$$m_l = l,\ l-1,\ \ldots,\ 0,\ \ldots,\ -l+1,\ -l \tag{12.67}$$

where E_n is given by (12.41). Thus, the **change in the energy** of a particular (n, l) state due to the presence of the magnetic field is

$$\boxed{\Delta E = m_l\left(\frac{e\hbar}{2m}\right)B = m_l\,\mu_B\,B} \tag{12.68}$$

Note that the magnetic interaction energy depends on the value of m_l. The reason is that m_l determines the orientation of the magnetic moment vector $\boldsymbol{\mu}$ with respect to the magnetic field **B**. This explains why m_l is called the magnetic quantum number.

Since there are $(2l + 1)$ values of m_l for a given value of l, an energy level with a particular l contains $(2l + 1)$ different orbital states. When no magnetic field is present, all these states have the same energy; that is, they are degenerate. In the presence of a magnetic field this degeneracy is removed and each l level is split into $(2l + 1)$ distinct energy levels. The adjacent levels differ in energy by $\mu_B\,B$. We have already shown this splitting in Figure 12.2. The splitting is very small even for fairly high magnetic fields because μ_B is very small. To get an estimate let $B = 2T$. Then

$$\mu_B\,B = 9.274 \times 10^{-24} \times 2\ \text{J}$$

$$= \frac{9.274 \times 2 \times 10^{-24}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 1.16 \times 10^{-4} \text{ eV}$$

This is very small compared to the atomic energy levels which have energies of the order of a few electron-volts. Because of the splitting of the energy levels, there is a consequent splitting of the spectral lines as we shall see below. But before that we mention the *selection rules* that govern the possible transitions.

Selection Rules

It can be shown by quantum mechanical calculations that not all combinations of final and initial levels are possible. Only those atomic transitions can take place in which the orbital quantum number l changes by ± 1 and the magnetic quantum number m_l does not change or changes by ± 1. That is, the **selection rules** for **allowed transitions** are:

$$\boxed{\begin{array}{l} \Delta l = \pm 1 \\ \Delta m_l = 0, \pm 1 \end{array} \quad \textbf{(Selection rules)}} \tag{12.69, 12.70}$$

There is no restriction on the changes in the principal quantum number n. Transitions which do not obey these rules are called **forbidden transitions.** Some forbidden transitions do occur but their probability is very small—the intensities of the corresponding spectral lines are about 10^4 times smaller than those of the lines given by allowed transitions.

The selection rules can be justified physically by invoking the conservation of angular momentum because the photon ordinarily carries one unit ($\hbar$) of angular momentum.

Splitting of Spectral Lines

It is clear from Figure 12.2 that the 1*s* state of hydrogen, for which $l = 0$, will not split, while the 2*p* state, for which $l = 1$, will split into three, with $m_l = +1, 0, -1$. The transitions from the three $l = 1$ states to a single $l = 0$ state will give radiation of three different frequencies. This is shown in Figure 12.4. All the transitions are allowed by the selection rules. Figure 12.4(a) shows the single line which is emitted when no magnetic field is applied. Figure 12.4(b) shows the three lines which appear when the field is applied. The frequency of one of the lines is equal to the original frequency ν_0. The frequencies of the other two lines are $\nu_0 - \Delta\nu$ and $\nu_0 + \Delta\nu$ where the frequency shift $\Delta\nu$ is

$$\boxed{\Delta\nu = \frac{\mu_B B}{h} = \left(\frac{e\hbar}{2m}\right)\frac{B}{h} = \frac{eB}{4\pi m} \quad \textbf{(Frequency shift)}} \tag{12.71}$$

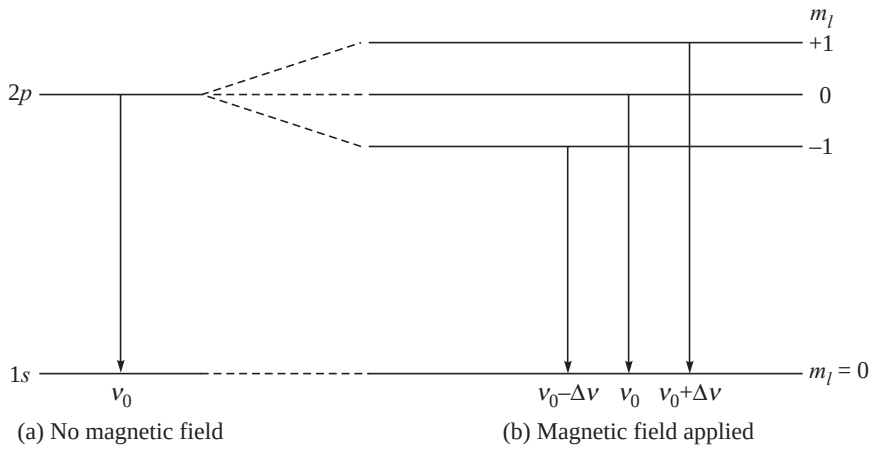


Figure 12.4 Splitting of the spectral line in the $2p \rightarrow 1s$ transition.

Let us now consider the $3d \rightarrow 2p$ transition. The $3d$ state, for which $l = 2$, will split into five states corresponding to $m_l = +2, +1, 0, -1, -2$. The transitions which are allowed by the selection rules are shown in Figure 12.5. It is seen that there are nine possible transitions. However, there are only three frequencies $\nu_0 - \Delta\nu$, ν_0 and $\nu_0 + \Delta\nu$, where $\Delta\nu$ is given by (12.71). Thus the $3d \rightarrow 2p$ line is also split into three lines only.

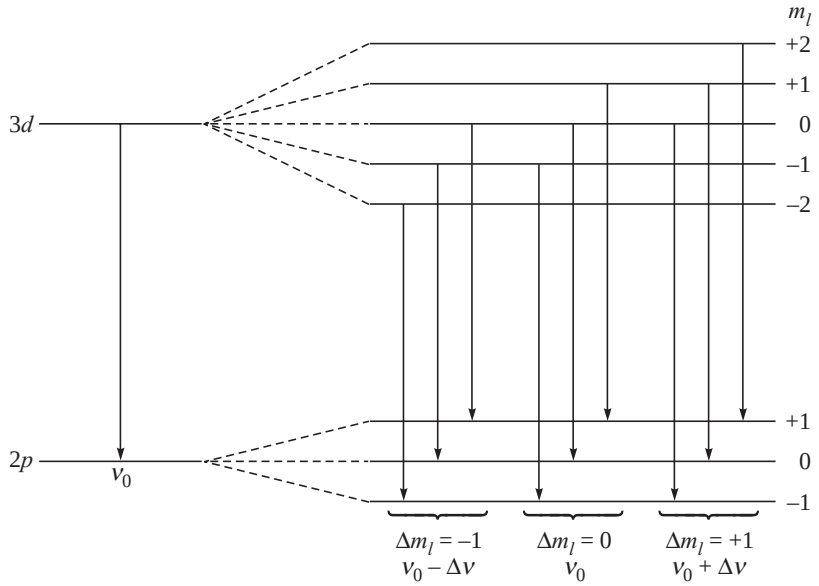


Figure 12.5 Splitting of the $3d \rightarrow 2p$ spectral line.

It is in general true for all atoms that if only the orbital angular momentum is considered then each line is split into three equispaced components. This is called the *normal* Zeeman effect.

SUMMARY

1. A potential $V(r)$ which depends only on the radial coordinate r and is independent of the angular variables θ, ϕ is called a spherically symmetric potential or a central potential.

2. For a spherically symmetric potential, the wave function $\psi(r, \theta, \phi)$ can be written as a product of two functions; a radial function $R(r)$ and an angular function $Y(\theta, \phi)$:

$$\psi(r, \theta, \phi) = R(r)\ Y(\theta, \phi)$$

3. The angular function, which is common to all central potentials, is the spherical harmonic $Y_{lm_l}(\theta, \phi)$ discussed in chapter 11. These are eigenfunctions of the operators L^2 and L_z with the eigenvalues $l(l + 1)\hbar^2$ and $m_l\hbar$ respectively, where $l = 0, 1, 2, \ldots$ and $m_l = l, l - 1, \ldots, 0, \ldots, -l + 1, -l$.

4. The radial function $R(r)$ satisfies the equation

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right]R(r) = 0$$

Its solution depends on the precise form of the potential $V(r)$.

5. For a hydrogenic atom, for which,

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

the normalized radial eigenfunctions are

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho),$$

where $$\rho = \left(\frac{2Zme^2}{n(4\pi\varepsilon_0)\hbar^2}\right)r$$

and $L_{n+l}^{2l+1}(\rho)$ is the associated Laguerre polynomial. n is called the principal quantum number and can have positive integral values.

6. The complete normalized energy eigenfunctions for a hydrogenic atom are

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)\ Y_{lm_l}(\theta,\phi)$$

where $n = 1, 2, 3, \ldots$
$l = 0, 1, 2, \ldots, n - 1$
$m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l$

7. The bound-state energies for the hydrogenic atom are

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{n^2} = -\frac{1}{2}mc^2\ \frac{(Z\alpha)^2}{n^2},$$

$$n = 1, 2, 3,\ldots,$$

where α is the fine structure constant.

The expression for E_n is same as that obtained in the Bohr model. The energy depends only on the principal quantum number n. Since for each n there are n^2 possible (lm_l) combinations, and hence as many eigenfunctions, the eigenvalues are n^2-fold degenerate. The m_l-degeneracy is due to spherical symmetry of $V(r)$; the l-degeneracy is characteristic of the Coulomb potential.

8. An electron orbiting around a nucleus in an atom behaves as a magnetic dipole of moment

$$\boldsymbol{\mu} = -\left(\frac{e}{2m}\right)\mathbf{L}$$

The quantity $e/2m$ is called the *gyromagnetic ratio.*

If the atom is placed in a magnetic field, this dipole experiences a torque and so there is a change in the energy of the electron. If the magnetic field B is along the z-axis, then the change in the energy of an (n, l) state is

$$\Delta E = \frac{e\hbar}{2m} Bm_l,\ m_l = l,\ l-1,\ \ldots,\ 0,\ \ldots,\ -l+1,\ -l.$$

Thus the energy of a state depends on m_l. Since there are $(2l + 1)$ values of m_l for a given l, an energy level with a particular l is split into $(2l + 1)$ distinct, close lying, energy levels. The adjacent levels differ in energy by $\mu_B B$ where $\mu_B = e\hbar/2m$ is called the *Bohr magneton.* As a consequence, there is a splitting of atomic spectral lines. This phenomenon is called the **Zeeman effect.**

9. The selection rules which govern the emission of spectral lines are

$$\Delta l = \pm 1$$

and

$$\Delta m_l = 0, \pm 1$$

According to these rules, each line is split into three components.The frequency of one of the lines is equal to the original frequency ν_0. The frequencies of the other two lines are $\nu_0 - \Delta\nu$ and $\nu_0 + \Delta\nu$ where $\Delta\nu = eB/4\pi m$. This is called the **normal Zeeman effect.** However, in most cases a line is split into more than three components. It is called the **anomalous Zeeman effect** and can be explained only after the *spin* of the electron is taken into account.

QUESTIONS

1. Obtain the time-independent Schrödinger equation in spherical polar coordinates for a particle in a spherically symmetric potential. Carry out the separation of variables and solve the angular equation.

2. Set up the time-independent Schrödinger equation for a hydrogenic atom in spherical polar coordinates (r, θ, ϕ). Split this equation into three equations corresponding to the three variables. Obtain the solution of the radial equation.

3. Write the Schrödinger equation for the hydrogen atom in terms of spherical polar coordinates (r, θ, ϕ) and separate the radial and angular parts. Solve the radial part to obtain the energy eigenvalues.

4. State the Schrödinger equation for the hydrogen atom in spherical coordinates. Explain the significance of various quantum numbers defining a state of the atom. What is the order of degeneracy of a certain energy level?

5. Solve the Schrödinger equation for a hydrogen-like atom and show that the expression obtained for energy levels is in agreement with Bohr's theory.

6. The radial wave function for the ground state ($n = 1$, $l = 0$) of the hydrogen atom is

$$R_{10}(r) = \left(\frac{1}{a_0}\right)^{3/2} 2e^{-r/a_0}$$

where $a_0 = \hbar^2/me^2$, the Bohr radius. If the probability of finding the electron between r and $r + dr$ is $P(r)\,dr$, draw a rough sketch to show how $P(r)$ varies with r for the ground state. Discuss briefly how the result compares with the prediction of Bohr's simple model of the hydrogen atom.

7. Show that the magnetic moment of an orbital electron is given by

$$\boldsymbol{\mu} = -\left(\frac{e}{2m}\right)\mathbf{L}$$

where the symbols have their usual meaning.

8. What is normal Zeeman effect? Discuss in detail how it is explained using quantum theory. Derive the expression for the frequency shift.

9. Consider the normal Zeeman effect in the $3d \rightarrow 2p$ transition. (a) Draw the energy-level diagram that shows the splitting of $3d$ and $2p$ levels in an external magnetic field. Indicate all possible transitions from each m_l state of $3d$ level to each m_l state of $2p$ level. (b) Which transitions satisfy the $\Delta m_l = \pm 1, 0$ selection rule? Show that there are only three different frequencies emitted.

Chapter

13 Atomic Structure I: One-Electron Atoms

Chapter Contents

13.1 Spin Angular Momentum
13.2 Magnetic Moment due to Spin
13.3 The Stern-Gerlach Experiment
13.4 Total Angular Momentum of the Electron in a One-Electron Atom
13.5 Spectroscopic Notation for Atomic States
13.6 Spin-Orbit Coupling and Fine Structure of Spectral Lines
13.7 Total Magnetic Moment of the Electron. The Landé *g* Factor
13.8 The Anomalous Zeeman Effect
13.9 Zeeman Splitting in a Strong Magnetic Field: The Paschen-Back Effect

In spite of the broad success of the quantum theory developed so far in predicting the energy levels and spectral lines of the hydrogen atom, it was soon realized that we were far from having a complete understanding of the structure and spectra of all the atoms.

Experimental data was continuously gathering which could not be explained on the basis of the existing theory. It was clear that some vital ingradients were missing from the theory. Since physics was in an active stage of development, these "ingradients" were very soon discovered leading to a satisfactory description of atomic structure and related phenomena. They were the concept of *electron spin* and the *Pauli exclusion principle*. We shall now study how these two hypotheses were incorporated into the theory to provide a resonably complete picture of atoms. The concept of spin will be incorporated into the theory in this chapter and the Pauli principle in the next chapter.

13.1 SPIN ANGULAR MOMENTUM

The main experimental observations which could not be accounted for by considering only the orbital angular momentum of the electron were the following:

The Anomalous Zeeman Effect

We have seen in chapter 12 that certain spectral lines split into a number of closely-spaced lines if the source is placed in a magnetic field. We found that if we attempt to explain this phenomenon considering the interaction of the orbital magnetic moment of the electron with the magnetic field, then each spectral line must be split into three components. However, in most cases a line is split into more than three lines. Since this splitting could not be understood, it was called the anomalous Zeeman effect.

Fine Structure of Spectral Lines

Even in the absence of a magnetic field, certain spectral lines actually consist of a group of closely-spaced lines. This *fine structure* is observed when the spectrum is examined with a spectrograph of high-resolving power. An example is the first line of the Balmer series of hydrogen which arises from the transition $n = 3 \rightarrow n = 2$. On the basis of the theory developed in chapter 12, this must be a single line of wavelength 6563 Å; actually there are two lines 1.4 Å apart. Another typical example is the yellow line of sodium—called the D-line—corresponding to the transition $4p \rightarrow 3s$ of the outermost electron. This line is found to be a doublet having wavelengths 5890 Å and 5896 Å. The fine structure is a small effect but it highlights the lack of completeness of the theory.

The Stern-Gerlach Experiment

In order to demonstrate the quantization of angular momentum, Stern and Gerlach passed a beam of neutral atoms through a non-uniform magnetic field. As we shall discuss a little later, if there were only orbital angular momentum, the beam must split into an odd number of different components. However, beams of some atoms were found to split into an even number of components which could not be explained.

In an attempt to account for these anomalies, two Dutch research scholars S. Goudsmidt and G. Uhlenbeck proposed, in 1925, that the *electron has an intrinsic angular momentum and associated with this angular momentum, a magnetic moment.* This is in addition to and independent of any orbital angular momentum that the electron has in an atom.

The intrinsic angular momentum is called *spin angular momentum*. The name spin gives the impression that the electron is a tiny charged sphere spinning about an axis. Surely, Goudsmidt and Uhlenbeck must have got the idea from the motion of a planet, which revolves around the sun as well as rotates

(spins) about its own axis. However, it was soon realized that this classical model of a rotating electron is not valid. In fact, spin has *no classical counterpart* and is a *purely quantum mechanical* effect. Of course, spin is not incorporated in the Schrödinger equation. However, in 1928 Dirac developed a more general equation combining quantum mechanics with relativity. The concept of spin appears in this theory naturally. All electrons have the same spin angular momentum whether they are free or bound in atoms. The spin is a fundamental property of the electron, like its charge and mass.

The spin angular momentum is described in terms of the **spin quantum number** *s*, usually called simply **spin**. The only value *s* can have is

$$\boxed{s = 1/2 \quad \textbf{(Spin quantum number)}} \tag{13.1}$$

This is in contrast to the orbital quantum number *l* whose value depends on the state of motion of the electron. The value $s = 1/2$ has been obtained empirically from spectroscopic data. It also follows from Dirac's relativistic theory of the electron. In this book, we shall not go into this theory.

The properties of the spin angular momentum are quite similar to those of the orbital angular momentum. The spin angular momentum is described by a vector **S** whose magnitude is given by

$$\boxed{S = \sqrt{s(s+1)}\,\hbar = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \frac{\sqrt{3}}{2}\hbar \quad \textbf{(Magnitude of spin angular momentum)}} \tag{13.2}$$

This is in analogy with the corresponding formula for the magnitude of the orbital angular momentum:

$$L = \sqrt{l(l+1)}\,\hbar$$

The *space quantization* of the spin angular momentum can be specified by giving its *z*-component S_z. This component is given in terms of the **spin magnetic quantum number** m_s. Recall that the orbital magnetic quantum number m_l can have $(2l + 1)$ values ranging from $-l$ to $+l$ in integer steps. Therefore, the vector **L** can have $(2l + 1)$ possible orientations with respect to the *z*-axis (In an actual experiment the *z*-axis is specified by applying a magnetic field in that direction; hence the name magnetic quantum number). Similarly, the spin angular momentum **S** can have $2s + 1 = 2(1/2) + 1 = 2$ orientations with respect to the *z*-axis. As such, the only allowed values of m_s are

$$\boxed{m_s = \pm 1/2 \quad \textbf{(Spin magnetic quantum number)}} \tag{13.3}$$

This is shown in Figure 13.1. The *z*-component of the spin angular momentum is, therefore,

$$\boxed{S_z = m_s\hbar = \pm\frac{1}{2}\hbar} \tag{13.4}$$

$S_z = +\frac{1}{2}\hbar$ is commonly called the "*spin up*" state and $S_z = -\frac{1}{2}\hbar$ is called the "*spin down*" state.

Thus, it turns out that *the complete description of the state of an electron in an atom requires four quantum numbers n, l, m_l* and m_s. The first three arise from the Schrödinger equation; the fourth one results from empirical evidence and also from the Dirac equation, which combines quantum mechanics with relativity.

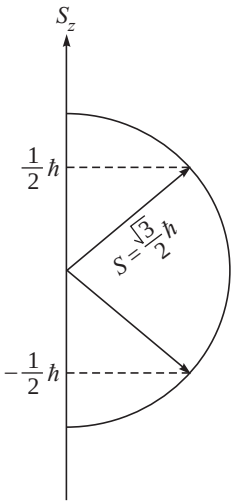


Figure 13.1 The two possible orientations of the spin angular momentum vector with respect to the *z*-axis.

Spin Eigenfunctions

A question that confronts us is how to write the spin wave function. Clearly, spin cannot be described by a spatial wave function of the type that describes an orbital angular momentum, i.e., a spherical harmonic. The reason is that there are no internal angles that can be marked. In the *matrix version of quantum mechanics*, the spin "up" ($m_s = +1/2$) and spin "down" ($m_s = -1/2$) eigenfunctions are given, respectively, by

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \; \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

The **complete wave function** for the hydrogen atom is then

$$\boxed{\Psi_{nlm_l m_s}(\mathbf{r}, \pm) = R_{nl}\, Y_{lm_l}(\theta, \phi)\, \chi_\pm}$$

The spin angular momentum operator is given, in matrix form, by

$$\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$$

where $\boldsymbol{\sigma}$ is called the *Pauli spin operator*. Its components have the matrix representation

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},\ \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix},\ \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

These are called the **Pauli spin matrices**. We shall not discuss these further in this book. The students will learn about these in their postgraduate studies.

Before ending this section, we would like to inform the reader that spin is an attribute associated with all the particles in nature: electrons, protons, neutrons, alpha particles, quarks, photons—all have a spin angular momentum which is a characteristic property of the particle and describes its behaviour. In fact on the basis of spin all the particles have been divided into two categories. The first category consists of those particles which have spin quantum number *s* equal to half an odd integer, i.e., 1/2, 3/2 etc. Such particles are called *fermions* because their distribution in solids is governed by the Fermi-Dirac statistics. The second category consists of particles which have spin quantum number *s* equal to zero or integer. Such particles are called *bosons* because their distribution is governed by the Bose-Einstein statistics. The electron, proton and neutron are fermions. The alpha particle and photon are bosons. An important difference between the two is that fermions obey the Pauli exclusions principle whereas bosons do not.

13.2 MAGNETIC MOMENT DUE TO SPIN

We have seen in section 12.4 that a magnetic moment is associated with the electron due to orbital angular momentum. It is given by (see Equation 12.61)

$$\boldsymbol{\mu}_L = -\frac{e}{2m}\mathbf{L} \tag{13.5}$$

By extrapolation, we might assume that there is a magnetic moment due to spin angular momentum as well. The assumption has proved to be correct. The magnetic moment due to spin is given by

$$\boxed{\boldsymbol{\mu}_S = -g_s \frac{e}{2m}\mathbf{S}} \quad \textbf{(Magnetic moment due to spin)} \tag{13.6}$$

Note the presence of the factor g_s which does not appear in Equation (13.5). This is purely a quantum mechanical factor that has no classical analogue. This factor has been obtained both experimentally as well as theoretically. The most recent experimental value is g_s = 2.000231930437. In Dirac's relativistic quantum theory, the magnetic moment due to spin emerged naturally, with g_s = 2, a value very close to the experimental value. The theoretical value calculated on the basis of quantum electrodynamics (QED) is 2.0002319305 which is in remarkable agreement with the experiment value.

Taking $g_s = 2$, the possible components of $\boldsymbol{\mu}_S$ along the z-axis are

$$\mu_{S_z} = \pm \frac{e\hbar}{2m} = \pm 1 \text{ Bohr magneton} \tag{13.7}$$

13.3 THE STERN-GERLACH EXPERIMENT

In 1922 O. Stern and W. Gerlach performed a series of experiments to verify directly the *space quantization of angular momentum*, i.e., the property that the angular momentum vector associated with a quantum state can take up only certain specified directions in space with respect to a chosen axis. However, the experiments also provided a confirmation of the hypothesis of *electron spin* proposed by Goudsmidt and Uhlenbeck.

Figure 13.2 shows the apparatus of the Stern-Gerlach experiment. A narrow beam of neutral atoms coming from an oven, after passing through collimating slits, are allowed to pass through a nonuniform magnetic field directed along the z-axis to finally fall on a collecting plate. The nonuniform magnetic field is produced by a magnet with specially designed pole pieces as shown in Figure 13.2(b). The upper pole piece is in the form of a knife edge and the lower one has a channel cut in it parallel to the knife edge. Thus the field has a gradient in the z-direction.

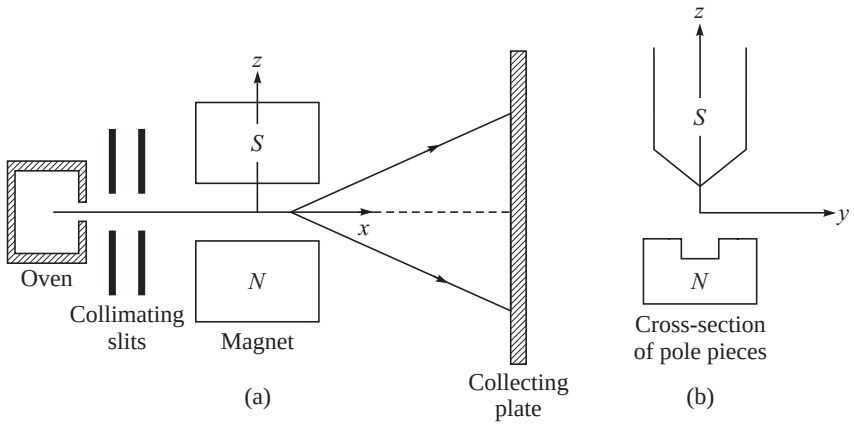
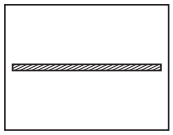


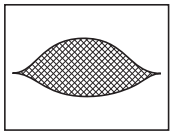
Figure 13.2 The Stern-Gerlach apparatus.

When no magnetic field is applied, the beam produces a single trace on the collecting plate as shown in Figure 13.3(a). When the field is switched on the trace splits distinctly into more than one trace. Let us discuss the theory of the experiment to be able to understand its outcome.

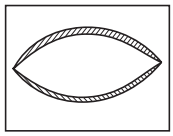
When the experiment was first performed, the concept of electron spin was not discovered. Let us ignore spin to begin with. Now, each atom consists of



(a) No magnet field



(b) Expected classical pattern with field on



(c) Actual pattern with field on

Figure 13.3 Pattern on the collecting plate for a beam of silver atoms.

electrons which have orbital angular momenta and hence magnetic moments. If $\boldsymbol{\mu}$ is the resultant magnetic moment of the atom and **B** is the applied magnetic field then the potential energy of the atom in the field is

$$U = -\boldsymbol{\mu}\cdot\mathbf{B} \tag{13.8}$$

Using Equation (12.61), we may write

$$U = \left(\frac{e}{2m}\right)\mathbf{L}\cdot\mathbf{B} \tag{13.9}$$

where **L** is the resultant orbital angular momentum of the atom.

Since the field is along the z-axis, $B = B_z$. Therefore, we obtain,

$$U = \frac{e}{2m}L_z\,B_z \tag{13.10}$$

The force on the atomic dipole is

$$F_z = -\frac{dU}{dz} = -\frac{e}{2m}L_z\frac{dB_z}{dz} \tag{13.11}$$

If space quantization of angular momentum did not exist, the **L** vectors for different atoms could be pointing in different directions in an arbitrary manner. Then L_z would take *any* value from $+L$ to $-L$ and, therefore, when the magnetic field is turned on, different atoms will move up or down by different amounts till they strike the collecting plate. The result would be a spreading out of the trace as shown in Figure 13.3(b). Stern and Gerlach found that this was not the case. On the other hand, the beam split into a few subbeams, each of which made a well defined separate trace on the plate. The number of traces depends on the type of atoms forming the beam. This could be possible *only if the angular momentum is quantized*. Let us see how. When L is quantized then the only possible values of L_z are given by $m_l\hbar$ where the magnetic quantum number m_l can take $(2l + 1)$ values ranging from $-l$ to $+l$, l being the orbital quantum number. Thus the beam must be split into $(2l + 1)$ subbeams.

However, there was a problem. Since $(2l + 1)$ is odd, it would imply that the number of traces on the plate would always be odd. It was found that this was not so for all atoms. For many atoms, e.g., silver, hydrogen, lithium, sodium, potassium, copper and gold it was found that the beam splits into two components, an even number (see Figure 13.3(c)). The explanation came only after the hypothesis of electron spin was proposed in 1925 because spin would also contribute to the magnetic moment of an electron.

Let us consider the case of silver. The valency of silver is one. It is now known that the orbital and spin magnetic moments of all but the valence electron in a silver atom cancel. For this electron the orbital angular momentum, and hence the orbital magnetic moment, is zero. Therefore, if spin were not there, a silver beam would not be split when the magnetic field is on, which is contrary to experimental observation.

Now, if spin is taken into account, it can take up only two orientations in a magnetic field, corresponding to $m_s = \pm 1/2$. Hence there would be two subbeams, which was actually observed. Thus, the Stern-Gerlach experiment was a direct confirmation of space quantization and the concept of electron spin.

PROBLEM 13.1 A beam of silver atoms moving with a velocity of 10^5 cm/s passes through a magnetic field of gradient 0.5 Wb/m^2/cm for a distance of 10 cm. What is the separation between the two components of the beam as it comes out of the magnetic field?

Solution: If the magnetic field is applied along the z-axis, then the force on the atom is along the z-axis and is given by (see Equation 13.11),

$$F = \mu_z \frac{dB_z}{dz}$$

where μ_z is the z-component of the magnetic moment of the atom.

A silver atom has only one valence electron which has $l = 0$ and therefore the magnetic moment is only due to spin. Therefore,

$$F = \mu_{S_z} \frac{dB_z}{dz}$$

Acceleration of the atom is

$$a_z = \frac{F}{M} = \frac{\mu_{S_z}}{M} \frac{dB_z}{dz}$$

where M is the mass of the silver atom. If d is the distance travelled inside the field and v is its velocity, then the time spent by the atom in the field is

$$t = \frac{d}{v}$$

The displacement of the atom along the z-direction is

$$z = \frac{1}{2} a_z t^2 = \frac{1}{2} \frac{\mu_{S_z}}{M} \cdot \frac{dB_z}{dz} \cdot \frac{d^2}{v^2}$$

From Equation (13.7)

$$\mu_{S_z} = \pm \frac{e\hbar}{2m}$$

The plus sign corresponds to electrons with spin "up" and the minus sign to electrons with spin "down". These two types of electrons will move in

opposite directions. Therefore, the separation between the two components of the beam

$$= 2z$$

$$= \frac{|\mu_{S_z}|}{M} \cdot \frac{dB_z}{dz} \cdot \frac{d^2}{v^2}$$

Now, $|\mu_{S_z}| = \frac{e\hbar}{2m}$ = 1 Bohr magneton

$= 9.274 \times 10^{-24}$ J/Wb/m^2

$M = 107.868$ amu

$= 107.868 \times 1.6605 \times 10^{-27}$ kg

$\frac{dB_z}{dz} = 0.5$ Wb/m^2/cm = 50 Wb/m^2/m

$d = 10$ cm $= 0.1$ m

$v = 10^5$ cm/s $= 10^3$ m/s

Substituting the values,

$$2z = 2.59 \times 10^{-3} \text{ m}$$

$$= \boxed{2.6 \text{ mm}}$$

13.4 TOTAL ANGULAR MOMENTUM OF THE ELECTRON IN A ONE-ELECTRON ATOM

In this section we consider hydrogen and hydrogen-like atoms which have only one electron moving around the nucleus. The case of more than one electron will be discussed in chapter 14.

As we have seen, the electron has both orbital angular momentum **L** and spin angular momentum **S**. The magnitude of **L** is given by

$$L = \sqrt{l(l+1)}\,\hbar \tag{13.12}$$

where l is the orbital angular momentum quantum number. The component of **L** along the z-axis is

$$L_z = m_l\hbar \tag{13.13}$$

where m_l is the orbital magnetic quantum number.

Similarly, the magnitude of **S** is given by Equation (13.2),

$$S = \sqrt{s(s+1)}\,\hbar$$

where s is the spin quantum number which has the value 1/2. The z-component of **S** is (Equation 13.4),

$$S_z = m_s\hbar$$

where m_s is the spin magnetic quantum number, having the values $\pm 1/2$.

The total angular momentum of the electron is the vector sum of **L** and **S**. It is denoted by the symbol **J**:

$$\boxed{\begin{array}{c}\mathbf{J} = \mathbf{L} + \mathbf{S} \\ \textbf{(Total angular momentum)}\end{array}} \tag{13.14}$$

The possible values of the magnitude of **J** are given in terms of the quantum number j by

$$\boxed{\begin{array}{c}J = \sqrt{j(j+1)}\,\hbar \\ \textbf{(Magnitude of J)}\end{array}} \tag{13.15}$$

where $$j = l + s \quad \text{or} \quad |l - s| \tag{13.16}$$

Since s is always 1/2,

$$j = l + \frac{1}{2} \quad \text{or} \quad \left| l - \frac{1}{2} \right| \tag{13.17}$$

Clearly, j is always half an odd integer. If $l = 0$, j has only the value 1/2. If $l = 1$, j can be 3/2 or 1/2. If $l = 2$, j can be 5/2 or 3/2, and so on.

The possible values of the component of **J** along the z-axis are given in terms of the quantum number m_j as

$$\boxed{J_z = m_j \hbar} \tag{13.18}$$

where

$$m_j = m_l \pm m_s \tag{13.19}$$

It can be easily seen that for a given value of j, m_j takes $(2j + 1)$ values given by

$$m_j = j,\ j - 1,\ \ldots,\ -(j - 1),\ -j \tag{13.20}$$

Thus we conclude that for a one-electron atom, the possible values of j are $l + \frac{1}{2}$ and $\left| l - \frac{1}{2} \right|$. The former corresponds to the case in which the vectors **L** and **S** have parallel z-components while the latter corresponds to **L** and **S** having antiparallel z-components. Figure 13.4 shows the two possible ways in which **J** can be formed by combining **L** and **S**. It must be kept in mind that the vectors **L** and **S** can never be parallel or antiparallel to each other or to the vector **J**.

In section 13.7 we shall see that the spin and the orbital motion produce internal magnetic fields. As a result the angular momenta **L** and **S** exert torques on each other. The effect of these torques is to make the vectors **L** and **S** precess around their resultant **J**, whose magnitude and direction are conserved in the absence of an external torque. This is shown in Figure 13.5(a). In case an external magnetic field **B** is present (which can be assumed to be along the

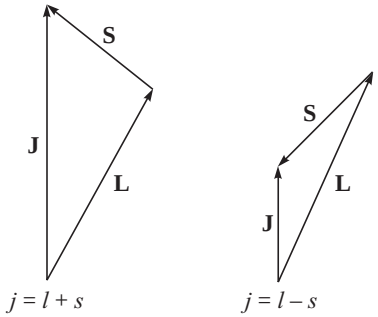


Figure 13.4 The two ways of combining **L** and **S** to form **J**.

z-axis), then the vector **J** precesses about the *z*-axis while **L** and **S** keep precessing about **J**, as shown in Figure 13.5(b).

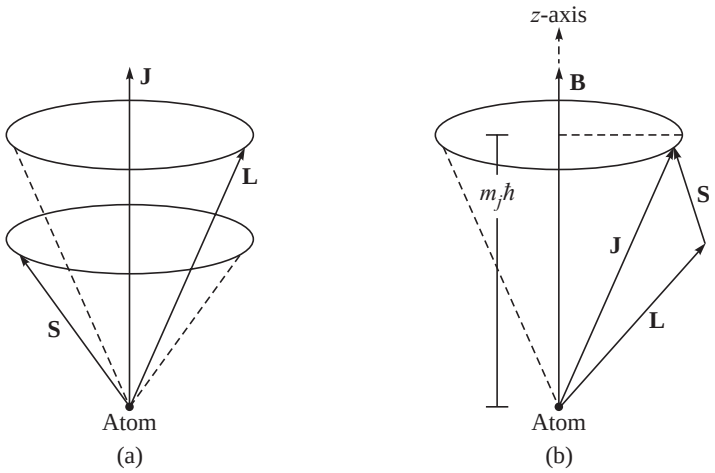


Figure 13.5 (a) Precession of **L** and **S** about **J** and (b) Precession of **J** about the direction of an external magnetic field **B** along the *z*-axis.

PROBLEM 13.2 Draw diagrams to show the possible orientations, with respect to the *z*-axis, of the vector **J** for the different *j*-states that correspond to $l = 1$.

Solution: The values of the quantum number j corresponding to $l = 1$ are:

$$j = 1 + \frac{1}{2} = \frac{3}{2} \quad \text{and} \quad j = 1 - \frac{1}{2} = \frac{1}{2}.$$

For the $j = \frac{1}{2}$ state, $m_j = \frac{1}{2}, -\frac{1}{2}$.

For the $j = \frac{3}{2}$ state, $m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$.

The possible orientations of **J** with respect to the *z*-axis for these *j* values are shown in Figure 13.6.

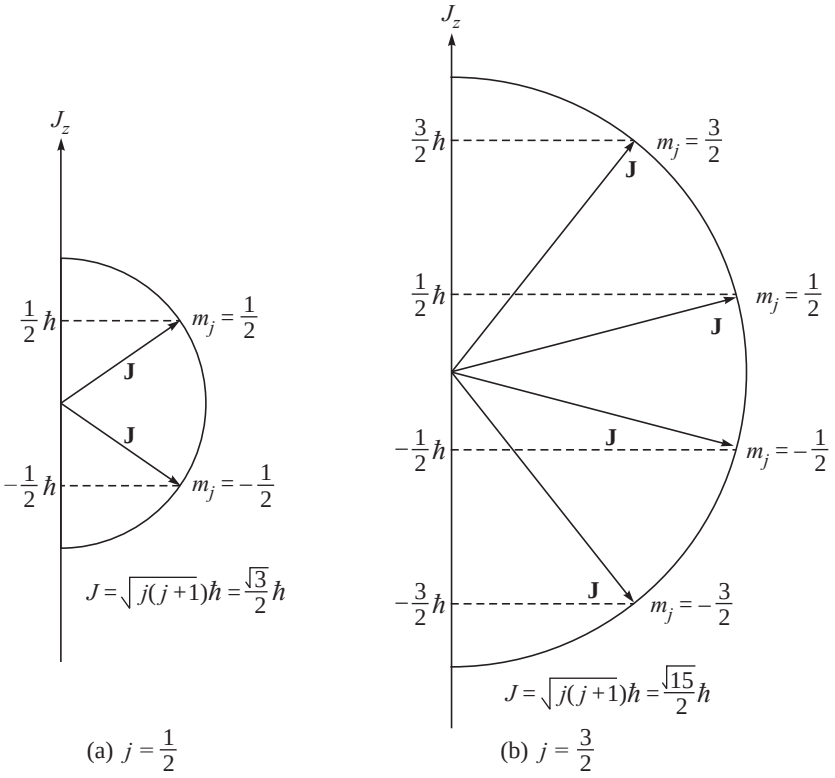


Figure 13.6 Space quantization of total angular momentum when $l = 1$.

13.5 SPECTROSCOPIC NOTATION FOR ATOMIC STATES

It would be appropriate at this stage to introduce the reader to the notation which spectroscopists commonly use to designate atomic states. This notation is also called **term notation** and is more useful in the case of *LS* coupling in multielectron atoms which will be discussed in section 14.8.

The term notation for a state is given by the following symbol:

$$\boxed{{}^{2s+1}\mathscr{L}_j}$$

Here *s* is the resultant spin quantum number of the atom and *j* is the total angular momentum quantum number. The symbol $\mathscr{L}$ denotes the letter corresponding to the resultant orbital angular momentum quantum number *l* according to following scheme.

Value of *l*	0	1	2	3	4	5	...
Letter ($\mathscr{L}$)	*S*	*P*	*D*	*F*	*G*	*H*	...

Recall from section 12.3 that lowercase letters *s*, *p*, *d*, *f* … etc. are used to denote the values of *l* for a single electron.

The superscript number $2s + 1$ is called the *multiplicity* of the state, which is the *number of different possible values of the total angular momentum J* obtained by various possible orientations of **L** and **S**.

Actually, the multiplicity is equal to $2s + 1$ only when $l > s$, since *j* has values ranging from $l + s$ to $l - s$ in integer steps. This is the usually occuring situation. The multiplicity corresponding to the case $s > l$ is $2l + 1$. As an example, let $l = 1$ and $s = \frac{3}{2}$. In this case the possible values of *j* are only three: $j = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. Thus the multiplicity is *three*. However, by convention, these states are designated ${}^4P_{5/2}$, ${}^4P_{3/2}$ and ${}^4P_{1/2}$ because $2s + 1 = 4$.

In the case of one-electron atoms or atoms having a single valence electron (e.g. sodium), the principal quantum number of this electron is sometimes attached as a prefix to the term symbol; that is, it is written as

$$\boxed{n\,{}^{2s+1}\mathscr{L}_j}$$

For example, the *ground state of a hydrogenic atom* has

$$n = 1,\ l = 0$$

Since *s* is always 1/2, we have $j = 1/2$. Therefore, the *term symbol* for this state is

$$\boxed{1\,{}^2S_{1/2} \quad \text{or} \quad \text{simply } {}^2S_{1/2}}$$
(Ground state of hydrogen)

As we shall see in Section 14.4, the *ground state of sodium* has

$$n = 3,\ l = 0$$

Therefore, its term symbol is

$$\boxed{3\,{}^2S_{1/2} \text{ or simply } {}^2S_{1/2}}$$
(Ground state of sodium)

Note that the *S*-state is always a singlet but the term notation indicates it as a doublet.

The *P* states of a one-electron atom are denoted by the term symbols

$${}^2P_{1/2},\ {}^2P_{3/2}$$

Similarly, the *D* and *F* states are denoted, respectively, by

$${}^2D_{3/2},\ {}^2D_{5/2}$$

and

$${}^2F_{5/2},\ {}^2F_{7/2}$$

Note that for a one-electron atom all the states for which $l \neq 0$ are doublets; i.e., they have two values of j.

PROBLEM 13.3 Write the values of the quantum numbers n, l, s, j, m_j for the following states:

$$3\ ^2P_{1/2},\ 3\ ^2D_{3/2},\ 4\ ^2F_{5/2}$$

Solution:

	n	l	s	j	m_j
$3^2P_{1/2}$	3	1	$\frac{1}{2}$	$\frac{1}{2}$	$\pm\frac{1}{2}$
$3^2D_{3/2}$	3	2	$\frac{1}{2}$	$\frac{3}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}$
$4^2F_{5/2}$	4	3	$\frac{1}{2}$	$\frac{5}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$

13.6 SPIN-ORBIT COUPLING AND FINE STRUCTURE OF SPECTRAL LINES

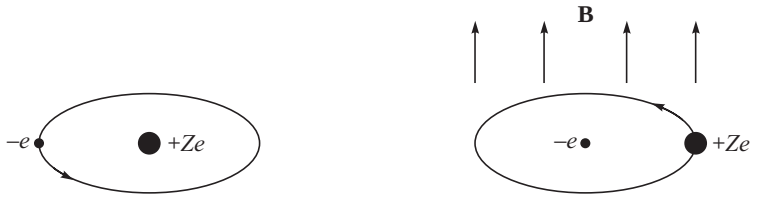
We can now understand the fine structure of spectral lines mentioned in section 13.1. Actually the splitting of spectral lines arises due to various effects. We shall be concerned here only with the splitting due to an interaction between the magnetic moments due to the spin and the orbital motion of the electron. This effect is called **spin-orbit coupling.**

The other effects which contribute to energy shifts and hence splitting of spectral lines are (i) the relativistic correction to the kinetic energy of the electron, (ii) the Darwin term which applies only to the $l = 0$ case, and (iii) the Lamb shift due to quantum electrodynamic effects known as radiative corrections. The energy shifts due to all these effects are of the same order of magnitude as due to spin-orbit coupling and, therefore, must be taken into account in a complete theory. However, these are beyond the scope of an undergraduate course.

A complete quantum mechanical derivation of the change in the energy of an atomic level due to spin-orbit interaction is outside the scope of this book. Therefore, we shall give a semiclassical treatment of this phenomenon.

Spin-orbit interaction can be understood in terms of the following simple model. An electron in an atom revolves around the nucleus. However, in the reference frame of the electron, it appears as if the nucleus is moving around it (Figure 13.7) (just as to an observer on the earth the sun appears to orbit the earth). Since the nucleus is a charged particle, this apparent motion generates a magnetic field at the location of the electron, as measured in the electron's frame of reference. This field interacts with the electron's spin magnetic moment. This causes a twofold splitting of the energy levels, corresponding to

the two possible orientations of the spin angular momentum. The splitting of energy levels results in a splitting of spectral lines. Hence the fine structure!



(a) An electron moving around a nucleus, as seen from the reference frame of the nucleus.

(b) In the reference frame of the electron, the nucleus appears to move around it. As a result, the electron experiences a magnetic field directed upwards.

Figure 13.7

We shall now show that the **spin-orbit interaction energy** can be expressed in terms of the scalar product of the orbital and spin angular momentum vectors **L** and **S**.

Consider a hydrogenic atom of atomic number Z. Assume that the electron is moving in a circular orbit of radius r with a speed v around the nucleus. In the reference frame of the electron, one sees the nucleus moving in a circular orbit of radius r with the same speed v but in a direction opposite to that of the electron. This is equivalent to a current loop with current I given by

$$I = \frac{Ze}{2\pi r/v} = \frac{Zev}{2\pi r}$$

The magnitude of the magnetic field due to this current at the centre of the loop is

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0 Zev}{4\pi r^2}$$

This is the magnetic field experienced by the electron. In vector notation,

$$\mathbf{B} = \frac{\mu_0 Ze}{4\pi r^2}\frac{\mathbf{r}\times\mathbf{v}}{r} = \frac{\mu_0 Ze}{4\pi mr^3}(\mathbf{r}\times m\mathbf{v})$$

$$= \frac{\mu_0 Ze}{4\pi mr^2}(\mathbf{r}\times\mathbf{p})$$

where m is the mass of the electron and $\mathbf{p}$ is its momentum. Putting $\mathbf{r}\times\mathbf{p} = \mathbf{L}$, the orbital angular momentum of the electron, and $\mu_0 = 1/\varepsilon_0 c^2$, we obtain

$$\mathbf{B} = \frac{Ze}{4\pi\varepsilon_0 mc^2 r^3}\mathbf{L} \tag{13.21}$$

If $\boldsymbol{\mu}_S$ is the magnetic moment of the electron due to spin, then the interaction energy of $\boldsymbol{\mu}_S$ and $\mathbf{B}$ is given by

$$H_{\text{spin-orbit}} = -\frac{1}{2}\,\boldsymbol{\mu}_S\cdot\mathbf{B} \tag{13.22}$$

The additional factor of 1/2 is known as the Thomas precession factor. Its explanation comes from a proper treatment using the theory of relativity. Substituting the value of $\boldsymbol{\mu}_S$ from Equation (13.6),

$$H_{\text{spin-orbit}} = -\frac{1}{2}\left(-g\frac{e}{2m}\mathbf{S}\right)\cdot\mathbf{B}$$

The value of the g factor is very very close to 2. Taking $g = 2$ and substituting for **B** from Equation (13.21),

$$H_{\text{spin-orbit}} = \frac{Ze^2}{8\pi\varepsilon_0 m^2c^2r^3}\ \mathbf{L}\cdot\mathbf{S} \tag{13.23}$$

Let us now introduce the total angular momentum of the electron:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

We have

$$J^2 = \mathbf{J}\cdot\mathbf{J} = (\mathbf{L} + \mathbf{S})\cdot(\mathbf{L} + \mathbf{S}) = L^2 + 2\mathbf{L}\cdot\mathbf{S} + S^2$$

or

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}(J^2 - L^2 - S^2) \tag{13.24}$$

Substituting in (13.23),

$$H_{\text{spin-orbit}} = \frac{Ze^2}{16\pi\varepsilon_0 m^2c^2r^3}\ (J^2 - L^2 - S^2) \tag{13.25}$$

So far, the treatment has been on classical lines. We can change to quantum mechanics by interpreting (13.25) as an operator corresponding to the spin-orbit interaction energy. If the electron is in a state described by the wave function ψ_{nlj} then the spin-orbit energy is given by

$$\begin{aligned} E_{\text{spin-orbit}} &= \langle H_{\text{spin-orbit}} \rangle \\ &= \frac{Ze^2}{16\pi\varepsilon_0 m^2c^2}\left\langle\frac{J^2 - L^2 - S^2}{r^3}\right\rangle \end{aligned} \tag{13.26}$$

where

$$\left\langle\frac{J^2 - L^2 - S^2}{r^3}\right\rangle = \int \psi^*_{nlj}\left(\frac{J^2 - L^2 - S^2}{r^3}\right)\psi_{nlj}\ dV \tag{13.27}$$

dV being an infinitesimal volume element. Now the eigenvalues of J^2, L^2 and S^2 are $j(j + 1)\hbar^2$, $l(l + 1)\hbar^2$ and $s(s + 1)\hbar^2$, where j, l and s are the total, orbital and spin angular momentum quantum numbers, respectively. Since $s = 1/2$,

$$s(s + 1)\hbar^2 = \frac{1}{2}\left(\frac{1}{2} + 1\right)\hbar^2 = \frac{3}{4}\hbar^2$$

Therefore, (13.26) becomes

$$E_{\text{spin-orbit}} = \frac{Ze^2\hbar^2}{16\pi\varepsilon_0 m^2c^2r^3}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\left\langle\frac{1}{r^3}\right\rangle \qquad (13.28)$$

The evaluation of $\left\langle\frac{1}{r^3}\right\rangle$ is somewhat lengthy and we shall not do it. The result is

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{Z^3}{a_0^3 n^3 l\left(l+\frac{1}{2}\right)(l+1)} \qquad (13.29)$$

where $$a_0 = 4\pi\varepsilon_0\hbar^2/(me^2) \qquad (13.30)$$

Substituting in (13.28) and using the fact that there are two possible values of j, viz., $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$, we obtain after some simplification,

$$\left.\begin{aligned} E_{\text{spin-orbit}} &= \frac{mc^2\,Z^4\alpha^4}{2n^3(l+1)(2l+1)} \quad \text{for } j = l + \frac{1}{2} \\ &= -\frac{mc^2\,Z^4\alpha^4}{2n^3 l(2l+1)} \quad \text{for } j = l - \frac{1}{2} \end{aligned}\right\} \qquad (13.31)$$

(Spin-Orbit Interaction Energy)

where α is the *fine structure constant*, given by

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137} \qquad (13.32)$$

For $l = 0$, the spin-orbit interaction vanishes and so $E_{\text{spin-orbit}} = 0$ in that case.

Equation (13.31) may also be written as

$$\left.\begin{aligned} E_{\text{spin-orbit}} &= -E_n\frac{Z^2\alpha^2}{n(l+1)(2l+1)} \quad \text{for } j = l + \frac{1}{2} \\ &= E_n\frac{Z^2\alpha^2}{nl(2l+1)} \quad \text{for } j = l - \frac{1}{2} \end{aligned}\right\} \qquad (13.33)$$

where E_n is the energy of the nth state when spin angular momentum is not considered. This is given in Equation (12.41):

$$E_n = -\frac{1}{2}mc^2\frac{Z^2\alpha^2}{n^2}$$

The **total energy** of a state designated by the quantum numbers n, l, j is now given by

$$E_{nlj} = E_n + (E_{\text{spin-orbit}})_{nlj}$$

Using (13.33) this becomes

$$\boxed{\begin{aligned} E_{nlj} &= E_n \left[1 - \frac{Z^2\alpha^2}{n(l+1)(2l+1)}\right] \quad \text{for } j = l + \frac{1}{2} \\ &= E_n \left[1 + \frac{Z^2\alpha^2}{nl(2l+1)}\right] \quad \text{for } j = l - \frac{1}{2} \end{aligned}} \tag{13.34}$$

We find that the spin-orbit interaction partially lifts the degeneracy which was present when this interaction was not included in our formulation. Earlier, the energy was found to depend only the principal quantum number n; now the energy depends on the orbital quantum number l too. In addition, there is a dependence on the total quantum number j as well.

For a given n and l, except $l = 0$, there are two states corresponding to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$. The spin-orbit interaction pushes up the $j = l + \frac{1}{2}$ state and pushes down the $j = l - \frac{1}{2}$ state from the unperturbed position. The **energy difference in the doublet**, using (13.31), is

$$\begin{aligned} (\Delta E)_{j=l\pm1/2} &= (E_{\text{spin-orbit}})_{j=l+1/2} - (E_{\text{spin-orbit}})_{j=l-1/2} \\ &= \frac{mc^2 Z^4\alpha^4}{2n^3(2l+1)}\left[\frac{1}{l+1} + \frac{1}{l}\right] \end{aligned}$$

or

$$\boxed{(\Delta E)_{j=l\pm1/2} = \frac{mc^2 Z^4\alpha^4}{2n^3 l(l+1)}} \tag{13.35}$$

The following conclusions can be immediately drawn:

1. The doublet separation decreases as n and l increase.
2. The doublet separation is relatively much more prominent in heavy atoms. It is proportional to Z^4.

Example: Hydrogen Atom

As an example of spin-orbit splitting consider the $n = 1$ and $n = 2$ levels of the hydrogen atom.

For $n = 1$, the only possible value of l is $l = 0$. The state is called 1s state. As discussed earlier there is no splitting for any s state.

For $n = 2$, the possible values of l are $l = 1, 2$. The corresponding states are 2s and 2p. There is no splitting for the 2s state. The 2p state is split into two,

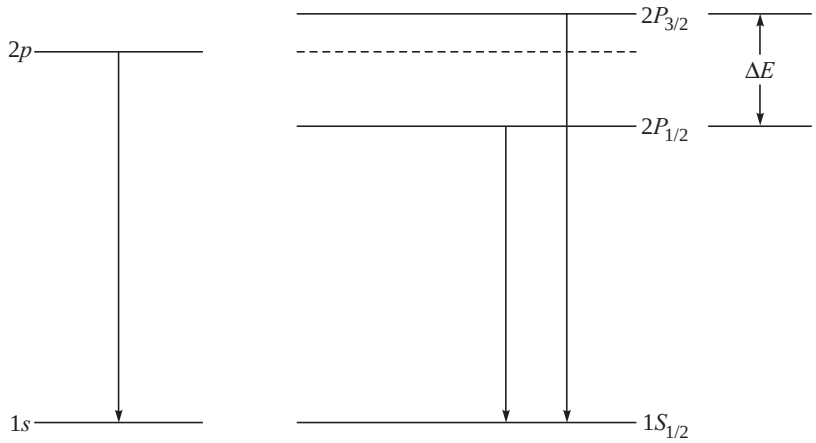
corresponding to $j = 1 + \frac{1}{2} = \frac{3}{2}$ and $j = 1 - \frac{1}{2} = \frac{1}{2}$. The two states are called $2\,P_{3/2}$ and $2\,P_{1/2}$. The $P_{3/2}$ state is pushed up and the $P_{1/2}$ state is pushed down by the spin-orbit interaction. The energy difference between the two states is obtained by substituting the values of the various quantities in Equation (13.35) and taking $Z = 1$:

$$\Delta E = \frac{(9.1\times10^{-31})\,(3\times10^{8})^{2}\,(1/137)^{4}}{2\,(2)^{3}1(1+1)}$$
$$= 7.264 \times 10^{-24}\ \text{J}$$
$$= 4.54 \times 10^{-5}\ \text{eV}$$

which is a very small amount.

It may be noted that the $P_{3/2}$ state is pushed up by $\Delta E/3$ and the $P_{1/2}$ state is pushed down by $2\Delta E/3$ from the unperturbed position.

As a result of this splitting the spectral line in the transition $2p \rightarrow 1s$ (which is the α line of the Lyman series) splits into two close lying lines corresponding to the $2P_{3/2} \rightarrow 1S_{1/2}$ and $2P_{1/2} \rightarrow 1S_{1/2}$ transitions. The situation is shown in Figure 13.8.



(a) Without spin-orbit coupling (single line).

(b) With spin-orbit coupling (two lines).

Figure 13.8 Splitting of the α line of the Lyman series in hydrogen spectrum.

In fact, each line of the Lyman series is split into a pair of lines called a *doublet*, corresponding to the transitions

$$nP_{3/2} \rightarrow 1S_{1/2},\ nP_{1/2} \rightarrow 1S_{1/2}$$

where $n > 1$.

The splitting of the lines in the Balmer and other series can be discussed in a similar manner. The situation is somewhat more complicated than the Lyman series and, in general, the lines are found to split into more than two components.

The **selection rules** for all such transitions are:

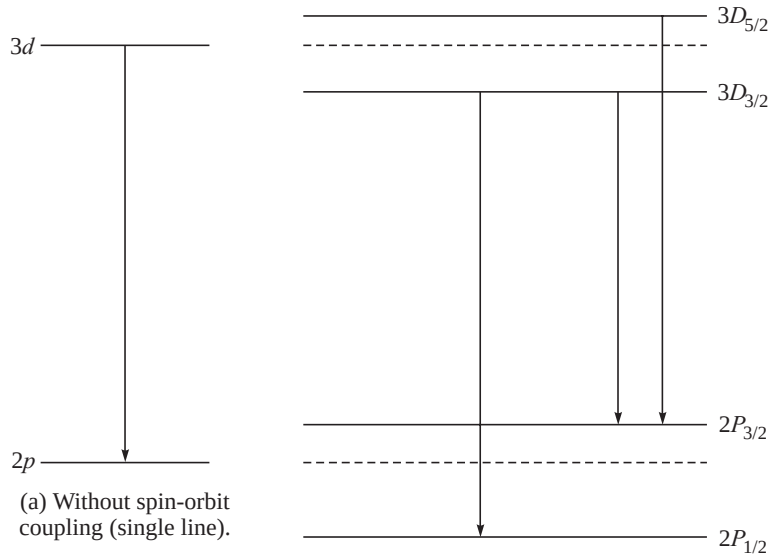
$$\boxed{\Delta l = \pm 1;\ \Delta j = 0, \pm 1} \tag{13.36}$$

PROBLEM 13.4 Show that the spectral line arising in the transition $3d \rightarrow 2p$ in the hydrogen atom splits into three components due to spin-orbit coupling.

Solution: The situation is shown in Figure 13.9. The spin-orbit interaction splits the $3d$ and $2p$ levels into doublets. The j values for the $3d$ level are 5/2 and 3/2 and, therefore, it splits into the states $3D_{5/2}$ and $3D_{3/2}$. The j values for the $2p$ level are 3/2 and 1/2 and it splits into the states $2P_{3/2}$ and $2P_{1/2}$. The selection rules allow the following three transitions

$$3D_{5/2} \rightarrow 2P_{3/2}$$
$$3D_{3/2} \rightarrow 2P_{3/2}$$
$$3D_{3/2} \rightarrow 2P_{1/2}$$

Thus the line will split into three components. Since the $3d$ splitting is much less than the $2p$ splitting, the first two lines are relatively close to each other than the third line.



(a) Without spin-orbit coupling (single line).

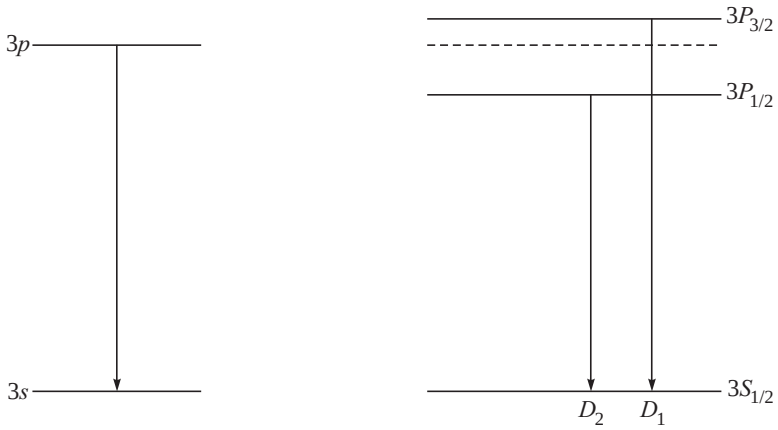
(b) With spin-orbit coupling (three lines).

Figure 13.9 Splitting of the $3d \rightarrow 2p$ line of the Balmer series in hydrogen spectrum.

PROBLEM 13.5 Show how the yellow line of sodium is split into two components (called D_1, D_2 lines) due to spin-orbit coupling.

Solution: Sodium has a single valence electron. In the ground state this electron is in the $3s$ level. The yellow light arises in the transition $3p \rightarrow 3s$. The

spin-orbit interaction splits the 3*p* level into two states—$3P_{3/2}$ and $3P_{1/2}$. The 3*s* level is not split—the corresponding *j*-state is $3S_{1/2}$. Thus there are two possible transitions: $3P_{3/2} \rightarrow 3S_{1/2}$ and $3P_{1/2} \rightarrow 3S_{1/2}$. As a result the yellow light is split into two components. The first one is called the D_1 line and the second is called the D_2 line. The situation is shown in Figure 13.10.



(a) Without spin-orbit coupling. (b) With spin-orbit coupling.

Figure 13.10 Splitting of the yellow line of sodium due to spin-orbit coupling.

13.7 TOTAL MAGNETIC MOMENT OF THE ELECTRON. THE LANDÉ *g* FACTOR

We have seen in sections 12.4 and 13.2 that the magnetic moment of the electron in an atom arises due to its orbital motion around the nucleus as well as due to its spin. The orbital magnetic moment is [Equation 12.61]

$$\boldsymbol{\mu}_L = -\left(\frac{e}{2m}\right)\mathbf{L} \tag{13.37}$$

and that due to the spin is [Equation 13.6]

$$\boldsymbol{\mu}_S = -g_s\left(\frac{e}{2m}\right)\mathbf{S}$$

Taking $g_s = 2$, we have,

$$\boldsymbol{\mu}_S = -2\left(\frac{e}{2m}\right)\mathbf{S} \tag{13.38}$$

The total magnetic moment of the electron is

$$\boldsymbol{\mu}_{LS} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) = -\frac{e}{2m}(\mathbf{J} + \mathbf{S}) \tag{13.39}$$

where **J** is the total angular momentum vector:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{13.40}$$

Figure 13.11 shows schematically the relationships between the angular momentum vectors and the magnetic moment vectors. The resultant magnetic moment $\boldsymbol{\mu}_{LS}$ (= $\boldsymbol{\mu}_L + \boldsymbol{\mu}_S$) is not along the line of the vector **J**. Since **L** and **S** precess about **J**, $\boldsymbol{\mu}_L$ and $\boldsymbol{\mu}_S$ must also precess about **J**. Hence their resultant $\boldsymbol{\mu}_{LS}$ also precesses about **J**. The effective magnetic moment of the electron will therefore be $\boldsymbol{\mu}_J$, the component of $\boldsymbol{\mu}_{LS}$ along the direction of **J**. The component perpendicular to **J** will average out to zero over one complete revolution. $\boldsymbol{\mu}_J$ may be written as

$$\boldsymbol{\mu}_J = (\boldsymbol{\mu}_{LS} \cdot \hat{\mathbf{J}})\, \hat{\mathbf{J}} \tag{13.41}$$

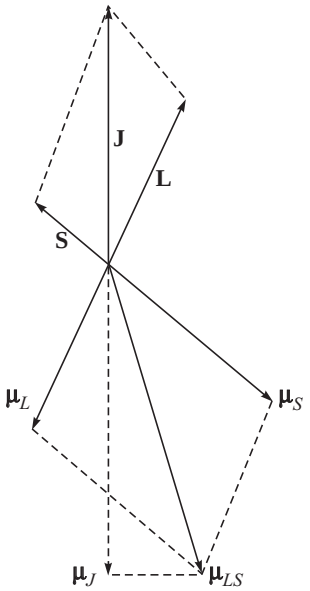


Figure 13.11 Schematic diagram showing the relationships between the angular momentum vectors and the magnetic moment vectors.

where $\hat{\mathbf{J}}$ is the unit vector along **J**:

$$\hat{\mathbf{J}} = \frac{\mathbf{J}}{J} \tag{13.42}$$

Substituting (13.42) into (13.41),

$$\boldsymbol{\mu}_J = \frac{(\boldsymbol{\mu}_{LS} \cdot \mathbf{J})\,\mathbf{J}}{J^2} \tag{13.43}$$

Using Equation (13.39),

$$\boldsymbol{\mu}_J = -\frac{e}{2m}\left(\frac{(\mathbf{J}+\mathbf{S})\cdot\mathbf{J}}{J^2}\right)\mathbf{J} \tag{13.44}$$

Let us now evaluate the quantity

$$g = \frac{(\mathbf{J} + \mathbf{S})\cdot\mathbf{J}}{J^2} \tag{13.45}$$

for a given (*lsj*) state. We have

$$(\mathbf{J} + \mathbf{S})\cdot\mathbf{J} = J^2 + \mathbf{S}\cdot\mathbf{J}$$

Since $\mathbf{L} = \mathbf{J} - \mathbf{S}$, we have,

$$L^2 = J^2 + S^2 - 2\,\mathbf{S}\cdot\mathbf{J}$$

or

$$\mathbf{S}\cdot\mathbf{J} = \frac{J^2 + S^2 - L^2}{2}$$

Therefore,

$$(\mathbf{J} + \mathbf{S})\cdot\mathbf{J} = J^2 + \frac{J^2 + S^2 - L^2}{2}$$

Substituting in (13.45),

$$g = 1 + \frac{J^2 + S^2 - L^2}{2J^2}$$

Replacing J^2, L^2 and S^2 by their quantum mechanical values $j(j + 1)\hbar^2$, $l(l + 1)\hbar^2$ and $s(s + 1)\hbar^2$, respectively, we obtain

$$\boxed{g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}} \quad \textbf{(Landé } \boldsymbol{g} \textbf{ factor)} \tag{13.46}$$

The quantity g is called the **Landé *g* factor**. Its value depends on the quantum numbers *l*, *s* and *j*. As such, its value is different for different states. The total magnetic moment of the electron can be written in terms of g as

$$\boxed{\boldsymbol{\mu}_J = -\frac{e}{2m} g\,\mathbf{J} = -g\mu_B \mathbf{J}/\hbar} \quad \textbf{(Total magnetic moment of the electron)} \tag{13.47}$$

where μ_B is the Bohr magneton.

PROBLEM 13.6 Calculate the Landé *g* factor and the total magnetic moment for the following states:

(a) $^2S_{1/2}$
(b) $^2P_{1/2}$
(c) $^2P_{3/2}$
(d) $^2D_{3/2}$

Solution: (a) For the $^2S_{1/2}$ state

$$l = 0,\ j = \frac{1}{2},\ 2s + 1 = 2 \Rightarrow s = \frac{1}{2}$$

Landé g factor $g = 1 + \dfrac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$

$$= 1 + \frac{\frac{1}{2}\cdot\frac{3}{2} + \frac{1}{2}\cdot\frac{3}{2} - 0{\cdot}1}{2\cdot\frac{1}{2}\cdot\frac{3}{2}}$$

$$= 1 + 1 = \boxed{2}$$

Total magnetic moment $\mu_J = g\sqrt{j(j+1)}\ \mu_B$

$$= 2\cdot\sqrt{\frac{1}{2}\cdot\frac{3}{2}}\ \mu_B$$

$$= \boxed{\sqrt{3}\,\mu_B}$$

where μ_B = 1 Bohr magneton = 9.274×10^{-24} Am^2

(b) For the $^2P_{1/2}$ state

$$l = 1,\ j = \frac{1}{2},\ s = \frac{1}{2}$$

$$g = 1 + \frac{\frac{1}{2}\cdot\frac{3}{2} + \frac{1}{2}\cdot\frac{3}{2} - 1{\cdot}2}{2\cdot\frac{1}{2}\cdot\frac{3}{2}}$$

$$= 1 - \frac{1}{3} = \boxed{\frac{2}{3}}$$

$$\mu_J = \frac{2}{3}\cdot\sqrt{\frac{1}{2}\cdot\frac{3}{2}}\,\mu_B = \boxed{\frac{1}{\sqrt{3}}\,\mu_B}$$

(c) For $^2P_{3/2}$ state

$$l = 1,\ j = 3/2 \Rightarrow s = \frac{1}{2}$$

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

$$= 1 + \frac{\frac{3}{2}\cdot\frac{5}{2} + \frac{1}{2}\cdot\frac{3}{2} - 1{\cdot}2}{2\cdot\frac{3}{2}\cdot\frac{5}{2}}$$

$$= 1 + \frac{1}{3} = \boxed{\frac{4}{3}}$$

$$\mu_J = g\,\mu_B\sqrt{j(j+1)}$$
$$= \frac{4}{3}\sqrt{\frac{3}{2}\cdot\frac{5}{2}}\;\mu_B$$
$$= \boxed{\frac{2}{3}\sqrt{15}\,\mu_B}$$

(d) For $^2D_{3/2}$ state

$$l = 2,\ j = \frac{3}{2},\ s = \frac{1}{2}$$
$$g = 1 + \frac{\frac{3}{2}\cdot\frac{5}{2} + \frac{1}{2}\cdot\frac{3}{2} - 2\cdot 3}{2\cdot\frac{3}{2}\cdot\frac{5}{2}}$$
$$= 1 - \frac{1}{5} = \boxed{\frac{4}{5}}$$
$$\mu_J = \frac{4}{5}\sqrt{\frac{3}{2}\cdot\frac{5}{2}}\,\mu_B$$
$$= \boxed{\frac{2}{3}\sqrt{15}\,\mu_B}$$

In Table 13.1 we list the values of the Landé g factor for some of the doublet states. Also given are the values of gm_j.

Table 13.1 Values of g and gm_j for Some Doublet States

State	l	j	g	m_j	gm_j
$^2S_{1/2}$	0	$\frac{1}{2}$	2	$\frac{1}{2}, -\frac{1}{2}$	$1, -1$
$^2P_{1/2}$	1	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{3}, -\frac{1}{3}$
$^2P_{3/2}$	1	$\frac{3}{2}$	$\frac{4}{3}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$2, \frac{2}{3}, -\frac{2}{3}, -2$
$^2D_{3/2}$	2	$\frac{3}{2}$	$\frac{4}{5}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$\frac{6}{5}, \frac{2}{5}, -\frac{2}{5}, -\frac{6}{5}$
$^2D_{5/2}$	2	$\frac{5}{2}$	$\frac{6}{5}$	$\frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$	$3, \frac{9}{5}, \frac{3}{5}, -\frac{3}{5}, -\frac{9}{5}, -3$

13.8 THE ANOMALOUS ZEEMAN EFFECT

We introduced the reader to the Zeeman effect in section 12.4. *The Zeeman effect is the splitting of spectral lines when the atom is placed in a magnetic*

field. The classical theory, due to Lorentz, predicted that each line must be split into three lines. The early quantum theory, which was developed before the electron spin was discovered, also agreed with the classical prediction. However, experimentally it was found that in a *weak* magnetic field, a spectral line is generally split into more than three lines. This effect was called the "anomalous" Zeeman effect, to distinguish it from the "normal" effect which could be explained by the theories existing at that point of time. We are now in a position to explain the anomalous Zeeman effect by taking into account the magnetic moment due to the spin of the electron.

Suppose the atom is placed in a magnetic field **B** which is relatively weak so that the coupling between **L** and **S** does not break down. In that case the total angular momentum vector **J** will precess about the direction of the magnetic field. The potential energy of the atom due to the action of the magnetic field would be

$$U = -\boldsymbol{\mu}_J \cdot \mathbf{B} \tag{13.48}$$

where $\boldsymbol{\mu}_J$ is the total magnetic moment of the electron. Substituting its value from Equation (13.47),

$$U = \left(\frac{g\,\mu_B}{\hbar} \right) \mathbf{J} \cdot \mathbf{B} \tag{13.49}$$

If the direction of the magnetic field is taken as the z-axis, then

$$U = \frac{g\,\mu_B}{\hbar} J_z B \tag{13.50}$$

Substituting for J_z its eigenvalue

$$m_j \hbar,\ m_j = j,\ j-1,\ \ldots,\ 0,\ \ldots,\ -(j-1),\ -j$$

we obtain the **shift in the energy** of the state with quantum numbers n, l, j, m_j as

$$\boxed{(\Delta E)_{nljm_j} = g\, m_j\, \mu_B\, B} \tag{13.51}$$

Thus the magnetic field removes the m_j-degeneracy. Earlier all the m_j states for a given set of n, l, j were degenerate. Now each (n, l, j) level is split into m_j levels. Consequently, each spectral line will be split into a number of lines, depending, of course, on the number of possible transitions, which are governed by the *selection rules*

$$\Delta l = \pm 1;\ \Delta m_j = 0, \pm 1 \tag{13.52}$$

It turns out that, due to the presence of the Landé g factor in (13.51), the splitting of the levels is different for different multiplets. As a result, there are more spectral lines in this case than the three lines corresponding to the normal Zeeman effect. To understand this, let us discuss the splittings in the case of the hydrogen atom.

Example: Hydrogen atom

We have seen in Figure 13.8 that the ground level of hydrogen is $1S_{1/2}$ and the next two levels are $2P_{1/2}$ and $2P_{3/2}$, the $P_{1/2}$ level being slightly lower than the $P_{3/2}$ level. The separation of the $P_{1/2}$ and $P_{3/2}$ levels is a consequence of the spin-orbit coupling. Thus, when no magnetic field is applied, there are two spectral lines resulting from the transitions $2P_{1/2} \rightarrow 1S_{1/2}$ and $2P_{3/2} \rightarrow 1S_{1/2}$ between these levels.

Let us see how the levels split in the presence of a magnetic field.

For the $1S_{1/2}$ level, we have from Table 13.1, $g = 2$. There are two possible values of m_j, $+\frac{1}{2}$ and $-\frac{1}{2}$. Therefore, this level splits into two. For $m_j = +\frac{1}{2}$, $gm_j = +1$ and for $m_j = -\frac{1}{2}$, $gm_j = -1$. Thus, according to (13.51) the energy shifts in the two levels are

$$\left.\begin{aligned}(\Delta E)_{m_j=\frac{1}{2}} &= \mu_B B \\ (\Delta E)_{m_j=-\frac{1}{2}} &= -\mu_B B\end{aligned}\right] \quad \text{and} \tag{13.53}$$

For the $2P_{1/2}$ level, $g = 2/3$. Again there are two possible values of m_j, $+\frac{1}{2}$ and $-\frac{1}{2}$ and so the level splits into two. For $m_j = \frac{1}{2}$, $gm_j = \frac{1}{3}$ and for $m_j = -\frac{1}{2}$, $gm_j = -\frac{1}{3}$. Therefore, the energy shifts of the two levels are

$$\left.\begin{aligned}(\Delta E)_{m_j=\frac{1}{2}} &= \frac{\mu_B B}{3} \\ (\Delta E)_{m_j=-\frac{1}{2}} &= \frac{-\mu_B B}{3}\end{aligned}\right] \quad \text{and} \tag{13.54}$$

For the $2P_{3/2}$ level, $g = 4/3$. There are four possible values of m_j:

$$m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$$

The corresponding values of gm_j are

$$gm_j = 2, \frac{2}{3}, -\frac{2}{3}, -2$$

The energy shifts of the four levels are

$$\left.\begin{aligned}(\Delta E)_{m_j=\frac{3}{2}} &= 2\mu_B B \\ (\Delta E)_{m_j=\frac{1}{2}} &= \frac{2\mu_B B}{3} \\ (\Delta E)_{m_j=-\frac{1}{2}} &= -\frac{2\mu_B B}{3} \\ (\Delta E)_{m_j=-\frac{3}{2}} &= -2\mu_B B\end{aligned}\right] \tag{13.55}$$

The energy splittings of the levels and the allowed transitions are shown in Figure 13.12. It is found that the $^2P_{1/2} \rightarrow {}^1S_{1/2}$ line splits into four lines and the $^2P_{3/2} \rightarrow {}^1S_{1/2}$ line splits into six lines.

The reason why there are more lines than in the case of the normal Zeeman effect is that the splittings of the levels are different for different multiplets. This is due to the fact that the values of the Landé g factor is different for different states.

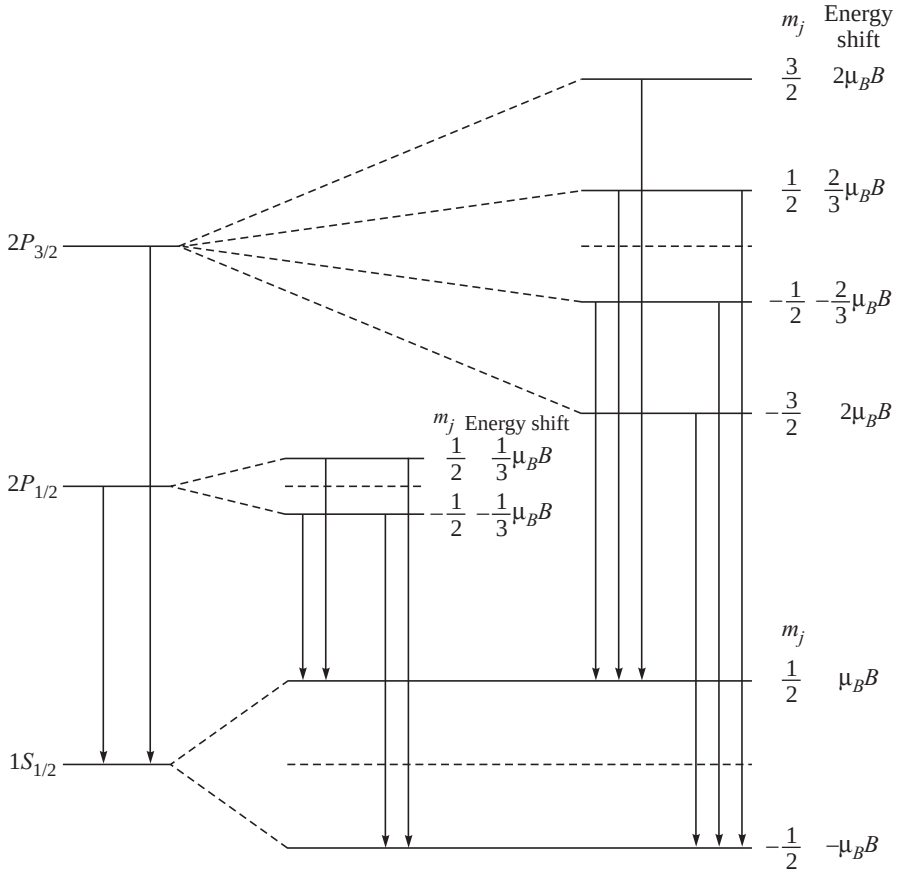


Figure 13.12 Splitting of the n = 1 and n = 2 levels and the corresponding spectral lines of atomic hydrogen in a weak magnetic field, giving rise to the anomalous Zeeman effect. The $^2P_{1/2} \rightarrow {}^1S_{1/2}$ line splits into four lines and the $^2P_{3/2} \rightarrow {}^1S_{1/2}$ line splits into six lines.

Frequencies of the Zeeman Lines

Let ν_0 be the frequency of a spectral line in the absence of the magnetic field. When the magnetic field is applied, the upper and lower levels will split into different m_j states. Let g, m_j and g', m_j' refer to a particular pair of upper and

lower states, respectively. Then the frequency ν_B of the spectral line arising due to the transition from the upper to the lower state is given by

$$\nu_B = \nu_0 + \frac{(gm_j - g'm_j')\mu_B B}{h} \tag{13.56}$$

or

$$\nu_B = \nu_0 + (gm_j - g'm_j')\frac{eB}{4\pi m} \tag{13.57}$$

Thus the **frequency shift** of this particular Zeeman component is

$$\boxed{\Delta\nu = (gm_j - g'm_j')\frac{eB}{4\pi m}} \tag{13.58}$$

13.9 ZEEMAN SPLITTING IN A STRONG MAGNETIC FIELD: THE PASCHEN-BACK EFFECT

As mentioned in the previous section, the anomalous Zeeman effect is observed in a weak magnetic field. *If the field is increased to a high value, it is found that the anomalous Zeeman pattern changes to the normal Zeeman triplet. This is called the Paschen-Back effect.* The reason for this behaviour can be understood as follows. When the atom is placed in a strong magnetic field, the spin-orbit coupling tends to break down. Therefore, the vectors **L** and **S** are uncoupled and the vector **J** ceases to exist. The vectors **L** and **S**, and hence the corresponding magnetic moment vectors $\boldsymbol{\mu}_L$ and $\boldsymbol{\mu}_S$, precess independently about **B**. They are, therefore, separately space-quantized. The potential energy of the atom due to the action of the magnetic field is now given by

$$\begin{aligned} U &= -\boldsymbol{\mu}_L\cdot\mathbf{B} - \boldsymbol{\mu}_S\cdot\mathbf{B} \\ &= -(\boldsymbol{\mu}_L + \boldsymbol{\mu}_S)\cdot\mathbf{B} \\ &= -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{B} \end{aligned} \tag{13.59}$$

If the direction of the magnetic field is taken as the *z*-axis, then the above expression becomes

$$U = -\frac{\mu_B}{\hbar}(L_z + 2S_z)B \tag{13.60}$$

Substituting for L_z its eigenvalue

$$m_l\hbar; \quad m_l = l,\ l\text{–}1,\ldots,\ 0,\ldots,\ -(l\text{–}1),\ -l \tag{13.61}$$

and for S_z its eigenvalue

$$m_s\hbar; \quad m_s = \pm\frac{1}{2} \tag{13.62}$$

we obtain the **energy shift** for the state with quantum numbers n, l, m_l, m_s as

$$\Delta E = (m_l + 2m_s)\ \mu_B\ B$$

Since $m_s = \pm 1/2$, this becomes

$$\Delta E = m_l \mu_B B \pm \mu_B B \tag{13.63}$$

It may be noted that the first term, which is due to orbital motion, is same as that in the case of the normal Zeeman effect. The second term, which is due to spin, is a constant for all the states. Therefore, when we calculate the energy change in a transition from one state to another, this term cancels out. Hence the pattern obtained is same as the normal Zeeman pattern.

In the above treatment we have completely neglected the spin-orbit coupling. However, more precise experimental and theoretical studies have shown that some spin-orbit coupling still remains. Consequently, each line of the Zeeman triplet is actually a doublet of very closely spaced lines.

PROBLEM 13.7 Draw the energy level diagram to show the Zeeman splittings of the ground state and the first two excited states of sodium in a weak magnetic field. Also show the transitions allowed by the selection rules.

Solution: Sodium has only one valence electron. Its ground state is $3\,^2S_{1/2}$ and the next two states are $3\,^2P_{1/2}$ and $3\,^2P_{3/2}$.

The anomalous Zeeman splittings and transitions are similar to those for the hydrogen atom shown in Figure 13.12.

SUMMARY

1. In 1925, Goudsmidt and Uhlenbeck proposed that the electron has an intrinsic spin angular momentum, and associated with it a magnetic moment. Spin has no classical counterpart and is a purely quantum mechanical effect. The spin quantum number s has the value 1/2 for electrons. Therefore, the magnitude of the spin angular momentum is

$$S = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar$$

The spin magnetic quantum number is $m_s = \pm 1/2$.
It was later realized that spin is associated with all the particles in nature. The particles which have $s = 1/2, 3/2\ldots$ etc. are called fermions and particles which have $s = 0, 1, \ldots$ etc. are called bosons.

2. The magnetic moment of the electron due to spin is

$$\boldsymbol{\mu}_S = -g_s \frac{e}{2m}\mathbf{S}$$

where $g_s \approx 2$.

3. The concept of spin made it possible to account for various unexplained phenomena, e.g., the anomalous Zeeman effect, the fine structure of spectral lines and the Stern-Gerlach experiment.

4. The total angular momentum **J** of the electron in an atom is the vector sum of **L** and **S**:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

The magnitude of **J** is

$$J = \sqrt{j(j+1)}\ \hbar$$

where $j = l + s$ or $|l - s|$

$$= l + \frac{1}{2} \quad \text{or} \quad \left| l - \frac{1}{2} \right|$$

j is called the total angular momentum quantum number. The corresponding magnetic quantum number has the values

$$m_j = j, j - 1, \ldots, -(j - 1), -j$$

5. The spectroscopic notation for atomic states is

$$^{2s+1}\mathscr{L}_j$$

where $\mathscr{L}$ is replaced by $S, P, D, F, \ldots$ etc. for $l = 0, 1, 2, 3, \ldots$ etc. The superscript $2s + 1$ is called the multiplicity of the state.

6. The interaction between the magnetic moments due to the spin and the orbital motion of the electron gives rise to spin-orbit coupling. This coupling pushes up the $j = l + \frac{1}{2}$ state and pushes down the $j = l - \frac{1}{2}$ state from the unperturbed position:

$$E_{\text{spin-orbit}} = \frac{mc^2 Z^4 \alpha^4}{2n^3 (l+1)(2l+1)} \quad \text{for} \quad j = l + \frac{1}{2}$$

$$= -\frac{mc^2 Z^4 \alpha^4}{2n^3 l(2l+1)} \quad \text{for} \quad j = l - \frac{1}{2}$$

Therefore the energy difference in the double is

$$(\Delta E)_{j=l\pm 1/2} = \frac{mc^2 Z^4 \alpha^4}{2n^3 l(l+1)}$$

This gives rise to the splitting of energy levels and hence the fine structure of spectral lines.

7. The total magnetic moment of the electron due to the combined effect of the orbital motion and the spin is

$$\boldsymbol{\mu}_J = -g\mu_B\ \mathbf{J}/\hbar$$

where the Landé g factor is

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

8. In a weak magnetic field, a spectral line is generally split into more than three lines. This is called the anomalous Zeeman effect.
In a weak magnetic field **B** the coupling between **L** and **S** does not breakdown and so the vector **J** precesses about the direction of **B**. The shift in the energy of the state with quantum numbers n, l, j, m_j is

$$(\Delta E)_{nljm_j} = g\ m_j\ \mu_B\ B$$

Thus each nlj level is split into m_j levels giving rise to splitting of spectral lines, subject to the selection rules

$$\Delta l = \pm 1,\ \Delta m_j = 0, \pm 1$$

9. If the magnetic field is increased to a high value, the anomalous pattern changes to the normal triplet. This is called the Paschen-Back effect. The reason is that in a strong field the spin-orbit coupling breaks down and therefore the vector **J** ceases to exist. The energy shift for the state n, l, m_l, m_s is

$$\Delta E = m_l\ \mu_B\ B \pm \mu_B\ B$$

The first term is due to orbital motion. The second term, which is due to spin, is constant and therefore, does not contribute to energy changes in a transition from one state to another. Hence the pattern becomes normal.

QUESTIONS

1. Describe the Stern-Gerlach experiment and give its theory. Discuss the significance of this experiment.

2. Describe an experiment which conclusively demonstrates the existence of spin angular momentum and explain how the experiment arrives at this conclusion.

3. Discuss diagrammatically the two possible ways in which the vectors **L** and **S** combine to form the vector **J**. Why do **L** and **S** precess around **J**?

4. What is meant by spin-orbit coupling? Obtain an expression for the energy difference in the two states corresponding to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ due to spin-orbit interaction.

5. What do you understand by fine-structure of spectral lines? Explain the splitting of the $2p \rightarrow 1s$ line in the hydrogen spectrum on the basis of spin-orbit coupling.

6. Show that the total magnetic moment of an orbital electron in the state with total angular momentum **J** is given by

$$\boldsymbol{\mu}_J = -g\ \mu_B\ \mathbf{J}/\hbar$$

Write the expression for the Landé g factor.

7. Distinguish between normal and anomalous Zeeman effect. Give the theory of the anomalous Zeeman effect.

8. Explain the splitting of atomic spectral lines in the presence of a moderate magnetic field by taking spin into account and hence explain the splitting of the $(2P_{3/2} \rightarrow 1S_{1/2})$ and $(2P_{1/2} \rightarrow 1S_{1/2})$ lines of the hydrogen spectrum in a moderate magnetic field.

Chapter

14 Atomic Structure II: Many-Electron Atoms

Chapter Contents

14.1 The Central Field Approximation
14.2 The Pauli Exclusion Principle
14.3 Symmetric and Antisymmetric Wave Functions: The Generalized Pauli Principle
14.4 Atomic Shell Structure
14.5 The Periodic Table
14.6 Explanation of the Periodic Table
14.7 Ionization Energies
14.8 Corrections to the Central Field Approximation: *LS* Coupling and *jj* Coupling

So far, our study of atomic structure has been mainly concerned with hydrogenic atoms, which have only a single electron moving around the nucleus. We have obtained the various quantum states of such an atom and their energies. Let us now move to atoms having more than one electron.

In order to obtain the quantum states and the corresponding energies of a many-electron atom, we have to solve the Schrödinger equation for this atom. However, the mathematical complexities of solving such an equation are so much that it has not been solved exactly even for the helium atom, which has only two electrons. The reason is that each of the electrons interacts not only with the nucleus but also with every other electron. Therefore, the potential energy and the wave function are functions of the coordinates of all the electrons. Obviously, the problem has to be solved under certain approximations.

The simplest approximation would be to ignore all interactions between electrons and consider each electron as moving only under the action of the

nucleus. This is called the *independent particle approximation.* However, it turns out that this approximation gives quantitative predictions which are far off the observed values. The reason is that as the number of electrons increases, their interactions with each other become as significant as their interactions with the nucleus.

14.1 THE CENTRAL FIELD APPROXIMATION

A more appropriate picture is to assume that *each electron moves in an effective spherically symmetric potential generated by all the other electrons and the nucleus.* This is called the central field approximation and provides a useful starting point for the understanding of the structure and properties of many-electron atoms.

The above approximation greatly simplifies the analysis because we can again deal with one-electron wave functions. The change is that the Coulomb potential energy function, which varies as $1/r$, is replaced by a different function $V(r)$. However, since $V(r)$ is spherically symmetric, it does not enter the differential equations for $\Theta(\theta)$ and $\Phi(\phi)$. Therefore, these angular functions, and hence the orbital angular momentum states, are the same as those for the hydrogenic atoms. The quantum numbers l and m_l have the same meaning as in one-electron atoms, and the magnitude and the z-component of the orbital angular momentum are again given by

$$L = \sqrt{l(l+1)}\,\hbar, \qquad l = 0, 1, 2, \ldots, n-1 \tag{14.1}$$

and

$$L_z = m_l\hbar, \qquad m_l = 0, \pm1, \pm2, \ldots, \pm l \tag{14.2}$$

The radial wave functions are, however, different from those for the hydrogenic atoms because of the change in $V(r)$. Therefore, the energy levels are not given by (12.41). It turns out that *the energy of a state now depends on both n and l, rather than just on n.* A quantum state can still be labelled by the four quantum numbers (n, l, m_l, m_s).

14.2 THE PAULI EXCLUSION PRINCIPLE

Having obtained the quantum states of a many-electron atom in the central-field approximation, the next, and perhaps the most important, question that confronts us is: *How are the electrons distributed in these states in the ground state of the atom*? In a hydrogenic atom, there is only one electron and it remains in the lowest energy state. Are all the electrons in a complex atom also packed in the lowest state? Experimental evidence tells us that this cannot be possible. For, if this were true, then there would be only gradual changes in the chemical and physical properties of elements as the atomic number increases. However, such gradual changes are not observed. The properties of elements are found

to vary drastically in certain cases where the atomic number differs by just one. A typical example is that of the three elements fluorine, neon and sodium, which have atomic numbers 9, 10 and 11, respectively. Fluorine is a halogen gas which is chemically very active and tends to form compounds in which each fluorine atom acquires an extra electron. Neon is an inert gas forming no compounds at all. Sodium is an alkali metal, which is also very active chemically and tends to form compounds in which each sodium atom loses an electron. There are similar other groups of elements.

These observations show that in the ground state of a many-electron atom all the electrons cannot be in the lowest energy level because in that case the chemical and physical properties cannot change so drastically by a small change in atomic number.

The answer to this puzzle was provided by W.Pauli, who in 1925, discovered the principle that governs the electronic structure of many-electron atoms. It is called the **exclusion principle** and states that

No two electrons in an atom can occupy the same quantum state.

Since an atomic state can be described by the four quantum numbers n, l, m_l and m_s, the exclusion principle may also be stated as

No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).

The Pauli exclusion principle has a more general and much deeper significance than what is apparent from the above discussion. Physicists have divided all particles into two classes: *fermions* and *bosons*. Particles having half-an-odd-integral spin are called *fermions* because a system of such particles is governed by the Fermi-Dirac statistical distribution law. Electrons, protons and neutrons are the most important examples of fermions.

Particles having zero or integral spin are called *bosons*. A system of such particles is governed by the Bose-Einstein statistical distribution law. Photons and alpha particles are examples of bosons.

It is found that only the fermions obey the Pauli exclusion principle. Thus, a more general statement of the exclusion principle is:

No two identical fermions in a system can occupy the same quantum state.

14.3 SYMMETRIC AND ANTISYMMETRIC WAVE FUNCTIONS: THE GENERALIZED PAULI PRINCIPLE

Before proceeding with the application of the exclusion principle in determining the electronic configuration of elements, let us see what are its implications in constructing the wave function of a system of identical particles. At the microscopic level, the identical particles are literally *indistinguishable* from one

another. There is simply no way to "tag" a particle so that it may be distinguished from another similar particle. This fact has to be taken care of in constructing the wave functions of identical particle systems. For simplicity, let us consider a two particle system. The particles are assumed to be noninteracting.

Suppose particle 1 is in the state labelled *a* and particle 2 is in the state labelled *b*. Then it would be natural to think that the two-particle wave function might be written as

$$\Psi(1,\ 2) = \psi_a(1)\ \psi_b(2) \tag{14.3}$$

Here the letter *a* or *b* represents the set of all the quantum numbers which define a particular one-particle state. For example, if the particles are electrons in an atom, then *a* or *b* represents the set (n, l, m_l, m_s). The integer 1 or 2 refers to all the coordinates of a particle.

On the other hand, if particle 2 is in state *a* and particle 1 is in state *b*, then the two-particle wave function would be

$$\Psi(2,\ 1) = \psi_a(2)\ \psi_b(1) \tag{14.4}$$

Now, since the particles are indistinguishable, neither of these wave functions is satisfactory because we have no way to find out which of the two describes the system at any moment. In fact, both the situations are equally probable. Therefore, the proper description of the system would be a linear combination of $\Psi(1, 2)$ and $\Psi(2, 1)$. Two such combinations are possible. The first is the **symmetric combination**

$$\begin{aligned}\Psi_S(1,\ 2) &= \frac{1}{\sqrt{2}}[\Psi(1,\ 2) + \Psi(2,\ 1)] \\ &= \frac{1}{\sqrt{2}}[\psi_a(1)\ \psi_b(2) + \psi_a(2)\ \psi_b(1)]\end{aligned} \tag{14.5}$$

The other is the **antisymmetric combination**

$$\begin{aligned}\Psi_A(1,\ 2) &= \frac{1}{\sqrt{2}}[\Psi(1,\ 2) - \Psi(2,\ 1)] \\ &= \frac{1}{\sqrt{2}}[\psi_a(1)\ \psi_b(2) - \psi_a(2)\ \psi_b(1)]\end{aligned} \tag{14.6}$$

The factor $1/\sqrt{2}$ in front is the normalization constant. $\Psi_S(1, 2)$ remains invariant when the two particles are exchanged while $\Psi_A(1, 2)$ changes sign under such an exchange. That is,

$$P_{12}\Psi_S(1,\ 2) = \Psi_S(2,\ 1) = \Psi_S(1,\ 2) \tag{14.7}$$

and

$$P_{12}\Psi_A(1,\ 2) = \Psi_A(2,\ 1) = -\Psi_A(1,\ 2) \tag{14.8}$$

where P_{12} is the *particle exchange operator.* The overall sign change is acceptable because physical probabilities involve only the absolute squares of the wave functions, which remain unaffected by a change of sign.

Now comes the important question: Which of the two wave functions, Ψ_S or Ψ_A must be used to describe a system of two identical particles. The answer is provided by the Pauli exclusion principle which says that *no two identical fermions in a system can occupy the same quantum state.* If, in violation of the Pauli principle, we put $a = b$ in the right hand sides of (14.5) and (14.6), we find that Ψ_A becomes zero whereas Ψ_S does not. Thus, the Pauli exclusion principle requires that only an antisymmetric wave function be used to describe a system of fermions, which includes electrons, the particles with which we are mainly concerned. The antisymmetric wave function for a two-fermion system [Equation (14.6)] may be written conveniently as a 2×2 determinant:

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1) & \psi_b(1) \\ \psi_a(2) & \psi_b(2) \end{vmatrix} \tag{14.9}$$

This form can be immediately generalized to write the antisymmetric wave function for any system of N fermions as an $N \times N$ determinant:

$$\Psi_A(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{a_1}(1) & \psi_{a_2}(1) & \ldots & \psi_{a_N}(1) \\ \psi_{a_1}(2) & \psi_{a_2}(2) & \ldots & \psi_{a_N}(2) \\ \vdots & & & \\ \psi_{a_1}(N) & \psi_{a_2}(N) & \ldots & \psi_{a_N}(N) \end{vmatrix} \tag{14.10}$$

This is called the ***Slater determinant.***

The other class of particles, *bosons,* have wave functions that are *symmetric* under exchange of any two identical particles.

It is found that it is more fundamental and useful to classify particles according to the symmetric or antisymmetric nature of their wave functions rather than according to whether they obey the Pauli exclusion principle or not. The **generalized Pauli principle** may be stated as:

The wave function of a many-particle system is antisymmetric under the exchange of two identical fermions and symmetric under the exchange of two identical bosons.

14.4 ATOMIC SHELL STRUCTURE

We are now in a position to determine how the electrons are distributed in various quantum states in a multielectron atom. This distribution is governed by the following two factors:

(1) The Pauli exclusion principle, according to which no two electrons can occupy the same quantum state.
(2) In a normal (unexcited) atom the electrons tend to occupy the lowest possible energy levels.

Shells and Subshells

A quantum state in an atom is characterized by four quantum numbers n, l, m_l and m_s. We have seen in section 14.1 that in the central field approximation, which we use for a multielectron atom, the energy of a state depends on the quantum numbers n and l, and not just on n. There is, of course, no dependence on m_l and m_s. The energy still depends mainly on n, as in a one-electron atom and varies only slightly with l. It increases (i.e. becomes less negative) as l is increased.

Electronic states having the same principal quantum number n are said to belong to the same **shell.** Shells are denoted by capital letters as under:

n	1	2	3	4	5	6	7
Letter	*K*	*L*	*M*	*N*	*O*	*P*	*Q*

This notation has its origin in the study of *X*-ray spectra. For a given n, the quantum states that have the same orbital quantum number l are said to belong to the same **subshell.** A subshell is denoted by the (n, l) values. Thus, we have 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d* etc. subshells. The maximum number of electrons in a subshell is $2(2l + 1)$, since the quantum number m_l can take the $(2l + 1)$ values ranging from $-l$ to $+l$ while m_s may be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

The total number of states with the principal quantum number n is given by

$$\begin{aligned} N &= \sum_{l=0}^{n-1} 2(2l + 1) \\ &= 2[1 + 3 + 5 + \ldots + (2n - 1)] \\ &= 2\left[n\left\{\frac{1+(2n-1)}{2}\right\}\right] \\ &= 2n^2 \end{aligned}$$

This is also the maximum number of electrons that can occupy the nth shell.

Table 14.1 gives the number of quantum states in, or equivalently, the maximum number of electrons that can occupy, all the shells and subshells upto $n = 4$.

It will be useful to keep in mind **some important facts** at this stage. The number of subshells in the nth shell is n. The number of *spin-orbitals* (defined by m_l, m_s) in a subshell with orbital quantum number l is $2(2l + 1)$. When a subshell is filled, $\Sigma m_l = \Sigma m_s = 0$. A completely filled shell or subshell is said to be "closed". For a closed subshell $L = S = 0$ and so $J = 0$. Therefore, only the electrons outside closed subshells need to be considered in order to find the total angular momentum of an atom.

Table 14.1 Number of Quantum States in Shells and Subshells upto $n = 4$

Shell		*Subshell*		*Number of States in the Subshell*	*Number of States in the Shell*
Notation	n	*Notation*	l	$2(2l + 1)$	$(2n^2)$
K	1	$1s$	0	2	2
L	2	$2s$	0	2	8
		$2p$	1	6	
M	3	$3s$	0	2	18
		$3p$	1	6	
		$3d$	2	10	
N	4	$4s$	0	2	32
		$4p$	1	6	
		$4d$	2	10	
		$4f$	3	14	

Electronic Configurations of Atoms in Their Ground States

A specification of the n and l values for all the electrons in an atom is called the electronic configuration for that atom. Unless otherwise stated, the electronic configuration means the ground state (lowest energy) configuration. The electronic configurations of all the elements can be obtained beginning with hydrogen and putting in the electrons one by one in the lowest available (n, l) state. It is found from spectroscopic analysis that the order of succession of the energy levels E_{nl} is nearly the same for all atoms and does not depend significantly on the details of the central field potential $V(r)$. From the analysis of spectroscopic data, the following empirical rule has been discovered, which governs the ascending order of energies E_{nl} of the (n, l) states:

The energy E_{nl} of an (n, l) state is an increasing function of the sum $(n + l)$. If two states have the same $(n + l)$ value then the state with the lower n value fills first: For example, the states $4p$ and $3d$ have the same $n + l$ value but $3d$ has lower n value. Therefore, $3d$ is filled before $4p$.

The order of the subshells with increasing energy is:

$1s$, $2s$, $2p$, $3s$, $3p$, [$4s$, $3d$], $4p$, [$5s$, $4d$], $5p$, [$6s$, $4f$, $5d$], $6p$, [$7s$, $5f$, $6d$].

The brackets enclose levels which have nearly the same energy so that their order can vary frome one atom to another.

In Table 14.2 we give the ground state electronic configurations of all the elements from $Z = 1$ to $Z = 103$. The number of electrons in a subshell is indicated by a superscript. Thus, $1s^2$ tells that there are 2 electrons in the $1s$ level and $2p^4$ tells that there are 4 electrons in the $2p$ level. The table also gives the lowest spectral terms and the ionization energies of the atoms.

For the first element hydrogen, which has $Z = 1$, the ground state configuration is $1s$ or $1s^1$. The next element, helium ($Z = 2$), has the ground state configuration $1s^2$. Thus helium has *closed* $1s$ subshell.

The third element, lithium (Z = 3), obviously has the ground state configuration $1s^2\ 2s$. This is written in the table as [He] 2*s*, where [He] indicates the He configuration, i.e., $1s^2$. This notation is used to indicate all inert gas configurations, e.g., [Ne], [Ar] etc.. Beryllium (Z = 4) has the closed subshell configuration $1s^2\ 2s^2$.

In the elements from boron (Z = 5) to neon (Z = 10), the electrons fill the 2*p* subshell progressively as shown in the table. The 2*p* subshell closes at neon which has the configuration [He] $2s^2\ 2p^6$.

From sodium (Z = 11) to argon (Z = 18) the normally expected filling process continues. At potassium (Z = 19) the first departure from the expected ordering according to lowest value of *n* occurs. The last electrons in potassium and calcium (Z = 20) go into the 4*s* rather than the 3*d* subshell.

The filling of the 3*d* subshell starts with scandium (Z = 21), which has the configuration [Ar] $4s^2\ 3d$, and ends with zinc (Z = 30). There is an anomaly at chromium (Z = 24) which has only one 4*s* electron, the configuration $4s3d^5$ being energetically more favourable than $4s^23d^4$. We have already mentioned that the 4*s* and 3*d* levels are very close in energy and their ordering may vary from element to element. In manganese (Z = 25) the last electron goes into the 4*s* level which was left unoccupied in chromium.

A similar situation develops at copper (Z = 29) and zinc (Z = 30) which have the configurations [Ar] $4s\ 3d^{10}$ and [Ar] $4s^2\ 3d^{10}$, respectively.

The rest of the table can be analyzed in a similar manner. The filling of the levels is generally systematic except for some irregularities at certain places.

Table 14.2 also gives the ionization energies and the lowest spectral terms for the elements for ready reference.

Table 14.2 Electronic Configurations, Spectral Terms and Ionization Energies of the Atoms in their Ground States

Atomic number Z	*Element*		*Electronic configuration*	*Spectral term*	*Ionization energy (eV)*
1	H	Hydrogen	1s	$^2S_{1/2}$	13.60
2	He	Helium	$1s^2$	$^1S_0$	24.59
3	Li	Lithium	[He]2*s*	$^2S_{1/2}$	5.39
4	Be	Beryllium	[He]$2s^2$	$^1S_0$	9.32
5	B	Boron	[He]$2s^22p$	$^2P_{1/2}$	8.30
6	C	Carbon	[He]$2s^22p^2$	$^3P_0$	11.26
7	N	Nitrogen	[He]$2s^22p^3$	$^4S_{3/2}$	14.53
8	O	Oxygen	[He]$2s^22p^4$	$^3P_2$	13.62
9	F	Fluorine	[He]$2s^22p^5$	$^2P_{3/2}$	17.42
10	Ne	Neon	[He]$2s^22p^6$	$^1S_0$	21.56
11	Na	Sodium	[Ne]3*s*	$^2S_{1/2}$	5.14
12	Mg	Magnesium	[Ne]$3s^2$	$^1S_0$	7.65
13	Al	Aluminium	[Ne]$3s^23p$	$^2P_{1/2}$	5.99
14	Si	Silicon	[Ne]$3s^23p^2$	$^3P_0$	8.15

(*Cont.*)

Table 14.2 Cont.

Atomic number Z	Element		Electronic configuration	Spectral term	Ionization energy (eV)
15	P	Phosphorus	[Ne]$3s^2 3p^3$	$^4S_{3/2}$	10.49
16	S	Sulphur	[Ne]$3s^2 3p^4$	$^3P_2$	10.36
17	Cl	Chlorine	[Ne]$3s^2 3p^5$	$^2P_{3/2}$	12.97
18	Ar	Argon	[Ne]$3s^2 3p^6$	$^1S_0$	15.76
19	K	Potassium	[Ar]$4s$	$^2S_{1/2}$	4.34
20	Ca	Calcium	[Ar]$4s^2$	$^1S_0$	6.11
21	Sc	Scandium	[Ar]$4s^2 3d$	$^2D_{3/2}$	6.54
22	Ti	Titanium	[Ar]$4s^2 3d^2$	$^3F_2$	6.82
23	V	Vanadium	[Ar]$4s^2 3d^3$	$^4F_{3/2}$	6.74
24	Cr	Chromium	[Ar]$4s 3d^5$	$^7S_3$	6.77
25	Mn	Manganese	[Ar]$4s^2 3d^5$	$^6S_{5/2}$	7.44
26	Fe	Iron	[Ar]$4s^2 3d^6$	$^5D_4$	7.87
27	Co	Cobalt	[Ar]$4s^2 3d^7$	$^4F_{9/2}$	7.86
28	Ni	Nickel	[Ar]$4s^2 3d^8$	$^3F_4$	7.64
29	Cu	Copper	[Ar]$4s 3d^{10}$	$^2S_{1/2}$	7.73
30	Zn	Zinc	[Ar]$4s^2 3d^{10}$	$^1S_0$	9.39
31	Ga	Gallium	[Ar]$4s^2 3d^{10} 4p$	$^2P_{1/2}$	6.00
32	Ge	Germanium	[Ar]$4s^2 3d^{10} 4p^2$	$^3P_0$	7.90
33	As	Arsenic	[Ar]$4s^2 3d^{10} 4p^3$	$^4S_{3/2}$	9.81
34	Se	Selenium	[Ar]$4s^2 3d^{10} 4p^4$	$^3P_2$	9.75
35	Br	Bromine	[Ar]$4s^2 3d^{10} 4p^5$	$^2P_{3/2}$	11.81
36	Kr	Krypton	[Ar]$4s^2 3d^{10} 4p^6$	$^1S_0$	14.00
37	Rb	Rubidium	[Kr]$5s$	$^2S_{1/2}$	4.18
38	Sr	Strontium	[Kr]$5s^2$	$^1S_0$	5.70
39	Y	Yttrium	[Kr]$5s^2 4d$	$^2D_{3/2}$	6.38
40	Zr	Zirconium	[Kr]$5s^2 4d^2$	$^3F_2$	6.84
41	Nb	Niobium	[Kr]$5s\, 4d^4$	$^6D_{1/2}$	6.88
42	Mo	Molybdenum	[Kr]$5s\, 4d^5$	$^7S_3$	7.10
43	Tc	Technetium	[Kr]$5s^2\, 4d^5$	$^6S_{5/2}$	7.28
44	Ru	Ruthenium	[Kr]$5s\, 4d^7$	$^5F_5$	7.37
45	Rh	Rhodium	[Kr]$5s\, 4d^8$	$^4F_{9/2}$	7.46
46	Pd	Palladium	[Kr]$4d^{10}$	$^1S_0$	8.34
47	Ag	Silver	[Kr]$5s\, 4d^{10}$	$^2S_{1/2}$	7.58
48	Cd	Cadmium	[Kr]$5s^2 4d^{10}$	$^1S_0$	8.99
49	In	Indium	[Kr]$5s^2 4d^{10} 5p$	$^2P_{1/2}$	5.79
50	Sn	Tin	[Kr]$5s^2 4d^{10} 5p^2$	$^3P_0$	7.34
51	Sb	Antimony	[Kr]$5s^2 4d^{10} 5p^3$	$^4S_{3/2}$	8.64
52	Te	Tellurium	[Kr]$5s^2 4d^{10} 5p^4$	$^3P_2$	9.01
53	I	Iodine	[Kr]$5s^2 4d^{10} 5p^5$	$^2P_{3/2}$	10.45
54	Xe	Xenon	[Kr]$5s^2 4d^{10} 5p^6$	$^1S_0$	12.13
55	Cs	Caesium	[Xe]$6s$	$^2S_{1/2}$	3.89
56	Ba	Barium	[Xe]$6s^2$	$^1S_0$	5.21
57	La	Lanthanum	[Xe]$6s^2 5d$	$^2D_{3/2}$	5.58
58	Ce	Cerium	[Xe]$6s^2 4f 5d$	$^1G_4$	5.47
59	Pr	Praseodymium	[Xe]$6s^2 4f^3$	$^4I_{9/2}$	5.42

(*Cont.*)

Table 14.2 Cont.

Atomic number Z	Element		Electronic configuration	Spectral term	Ionization energy (eV)
60	Nd	Neodymium	$[Xe]6s^2 4f^4$	$^5I_4$	5.49
61	Pm	Promethium	$[Xe]6s^2 4f^5$	$^6H_{5/2}$	5.55
62	Sm	Samarium	$[Xe]6s^2 4f^6$	$^7F_0$	5.63
63	Eu	Europium	$[Xe]6s^2 4f^7$	$^8S_{7/2}$	5.67
64	Gd	Gadolinium	$[Xe]6s^2 4f^7 5d$	$^9D_2$	6.14
65	Tb	Terbium	$[Xe]6s^2 4f^9$	$^6H_{15/2}$	5.85
66	Dy	Dysprosium	$[Xe]6s^2 4f^{10}$	$^5I_8$	5.93
67	Ho	Holmium	$[Xe]6s^2 4f^{11}$	$^4I_{15/2}$	6.02
68	Er	Erbium	$[Xe]6s^2 4f^{12}$	$^3H_6$	6.10
69	Tm	Thulium	$[Xe]6s^2 4f^{13}$	$^2F_{7/2}$	6.18
70	Yb	Ytterbium	$[Xe]6s^2 4f^{14}$	$^1S_0$	6.25
71	Lu	Lutetium	$[Xe]6s^2 4f^{14} 5d$	$^2D_{3/2}$	5.43
72	Hf	Hafnium	$[Xe]6s^2 4f^{14} 5d^2$	$^3F_2$	7.0
73	Ta	Tantalum	$[Xe]6s^2 4f^{14} 5d^3$	$^4F_{3/2}$	7.89
74	W	Tungsten	$[Xe]6s^2 4f^{14} 5d^4$	$^5D_0$	7.98
75	Re	Rhenium	$[Xe]6s^2 4f^{14} 5d^5$	$^6S_{5/2}$	7.88
76	Os	Osmium	$[Xe]6s^2 4f^{14} 5d^6$	$^5D_4$	8.7
77	Ir	Iridium	$[Xe]6s^2 4f^{14} 5d^7$	$^4F_{9/2}$	9.1
78	Pt	Platinum	$[Xe]6s\,4f^{14} 5d^9$	$^3D_3$	9.0
79	Au	Gold	$[Xe]6s\,4f^{14} 5d^{10}$	$^2S_{1/2}$	9.23
80	Hg	Mercury	$[Xe]6s^2 4f^{14} 5d^{10}$	$^1S_0$	10.44
81	Tl	Thallium	$[Xe]6s^2 4f^{14} 5d^{10} 6p$	$^2P_{1/2}$	6.11
82	Pb	Lead	$[Xe]6s^2 4f^{14} 5d^{10} 6p^2$	$^3P_0$	7.42
83	Bi	Bismuth	$[Xe]6s^2 4f^{14} 5d^{10} 6p^3$	$^4S_{3/2}$	7.29
84	Po	Polonium	$[Xe]6s^2 4f^{14} 5d^{10} 6p^4$	$^3P_2$	8.42
85	At	Astatine	$[Xe]6s^2 4f^{14} 5d^{10} 6p^5$	$^2P_{3/2}$	9.5
86	Rn	Radon	$[Xe]6s^2 4f^{14} 5d^{10} 6p^6$	$^1S_0$	10.75
87	Fr	Francium	$[Rn]7s$	$^2S_{1/2}$	4.0
88	Ra	Radium	$[Rn]7s^2$	$^1S_0$	5.28
89	Ac	Actinium	$[Rn]7s^2 6d$	$^2D_{3/2}$	6.9
90	Th	Thorium	$[Rn]7s^2 6d^2$	$^3F_2$	
91	Pa	Protactinium	$[Rn]7s^2 5f^2 6d$	$^4K_{11/2}$	
92	U	Uranium	$[Rn]7s^2 5f^3 6d$	$^5L_6$	4.0
93	Np	Neptunium	$[Rn]7s^2 5f^4 6d$	$^6L_{11/2}$	
94	Pu	Plutonium	$[Rn]7s^2 5f^6$	$^7F_0$	5.8
95	Am	Americium	$[Rn]7s^2 5f^7$	$^8S_{7/2}$	6.0
96	Cm	Curium	$[Rn]7s^2 5f^7 6d$	$^9D_2$	
97	Bk	Berkelium	$[Rn]7s^2 5f^8 6d$	$^8H_{17/2}$	
98	Cf	Californium	$[Rn]7s^2 5f^{10}$	$^5I_8$	
99	Es	Einsteinium	$[Rn]7s^2 5f^{11}$	$^4I_{15/2}$	
100	Fm	Fermium	$[Rn]7s^2 5f^{12}$	$^3H_6$	
101	Md	Mendelevium	$[Rn]7s^2 5f^{13}$	$^2F_{7/2}$	
102	No	Nobelium	$[Rn]7s^2 5f^{14}$	$^1S_0$	
103	Lw	Lawrencium	$[Rn]7s^2 5f^{14} 6d$	$^2D_{3/2}$	

In section 14.6, we shall see how the electronic structure of elements accounts for the periodicity and regularity in their properties. Before that, in section 14.5, we present the main features of the periodic table of elements, which was drawn up by the chemists on the basis of chemical properties.

14.5 THE PERIODIC TABLE

The Russian chemist D. I. Mendeleev formulated the **periodic law** of elements in 1869, which states that

> **When the elements are arranged in order of increasing atomic number, the elements with similar physical and chemical properties recur at regular intervals.**

Mendeleev arranged all the elements according to increasing atomic number in a table such that the elements with similar properties appear in a column. The elements in a row are found to exhibit gradual changes in properties as one proceeds from the first to the last element in the row. *The arrangement is called the periodic table.* A simple modern version of the periodic table is given in Table 14.3.

The elements in a column are said to form a **group** and the elements in a row are said to form a **period.** Group I consists of hydrogen and the alkali metals. Group II consists of alkaline earth metals. Group VII consists of halogen gases and Group VIII consists of inert (noble) gases. Thus, across each period there is a gradual transition from an active (alkali) metal through less active metals and nonmetals to highly active nonmetals (halogen) and finally to an inert gas.

Each period after the third has a series of elements, called **transition metals.** They have similar physical and chemical properties. Fifteen of the transition metals in period 6, known as **lanthanides** (or **rare earths**), are almost indistinguishable in their properties. They are put at the same place in the periodic table. Similarly, period 7 has a group of metals, called **actinides** which are almost indistinguishable, and hence placed at the same place.

14.6 EXPLANATION OF THE PERIODIC TABLE

When Mendeleev proposed the periodic table in 1869, electrons and nuclei were not discovered and quantum mechanics was a long way off in the future. After the development of the quantum theory of the atom, it was realized that the concept of electronic shells and subshells fits extremely well into the pattern of the periodic table. We now know that the chemical activity of an atom is mainly determined by the electrons in the 'outer' subshell, which are least tightly bound. These are called the *valence* electrons. The crucial factors are the number of occupied states in this subshell, and the energy difference (gap) between this subshell and the next one.

Table 14.3 The Periodic Table

Group	I	II											III	IV	V	VI	VII	VIII
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57–71 †	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89–103 ††														*Halogens*	*Inert gases*
	Alkali metals																	
	† Rare earths (Lanthanides)			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
	†† Actinides			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

An atom tends to be chemically inactive if its outer subshell is completely filled (closed) and there is a large energy gap between this subshell and the next higher one. This is the situation for the gases He, Ne, Ar, Kr, Xe and Rn. Hence the reason why they are called *inert* or *noble* gases. In the periodic table all of them appear in a single column (group VIII).

The alkali metals, Li, Na, K, Rb, Cs and Fr contain a single *s* electron outside an 'inert gas' core. This electron is relatively far from the nucleus and is also 'shielded' from the nucleus by the inner electrons. Therefore, it is weakly bound and the atom has a tendency to lose this electron in its interaction with other atoms. They all appear in the same column (group I) in the periodic table.

At the other extreme are halogens, F, Cl, Br and I, which have an outer *p* subshell lacking only one electron. They have a tendency to capture an electron so that they may complete their outer subshells and thus have a more stable arrangement of electrons. This makes them chemically very active. This explains why a halogen atom readily combines with an alkali atom to form compounds such as NaCl, LiF etc. The halogens appear in group VII of the periodic table.

We can account for the similarities of the elements in the other groups of the periodic table by the same kind of reasoning. Thus, *the recurrence of similar chemical properties in the periodic table is due to the regularities in the electronic configuration of outer electronic shells.* This phenomenon is basically a consequence of the Pauli exclusion principle.

The transition elements are formed when a *d* state is gradually filled. In these elements, the outer electrons have configurations of the type $(n+1)s^2nd^x$ or $(n+1)snd^{x+1}$. The first set of transition elements (from $Z = 21$ to $Z = 30$) has $n = 3$, the second set (from $Z = 39$ to $Z = 48$) has $n = 4$, and the third set (from $Z = 71$ to $Z = 80$) has $n = 5$. Some irregularities occur in the filling of subshells due to the competition between the nd and $(n+1)s$ levels.

The *lanthanides* (rare earths) correspond to the gradual filling of the $4f$ subshell and the *actinides* to the filling of the $5f$ subshell, with some irregularities in both the cases. The addition of the *f* electrons has very little effect on the chemical properties of these elements. This justifies these being put at the same place in the periodic table.

Thus, all the salient features of the periodic table can be accounted for by the quantum theory of atomic structure.

14.7 IONIZATION ENERGIES

The ionization energy of an atom is the energy required to remove the outermost electron from the atom. In Figure 14.1 we show the variation of the ionization energies of the elements with the atomic number *Z*. As expected, the ionization energy does not vary in a monotonic manner with *Z*. It has maximum values for the inert gases which have a complete *K* shell (He) or *p* subshell (Ne, Ar, Kr, Xe, Rn) and is minimum for the alkali metals whose electronic configuration corresponds to that of an ideal gas plus an s electron.

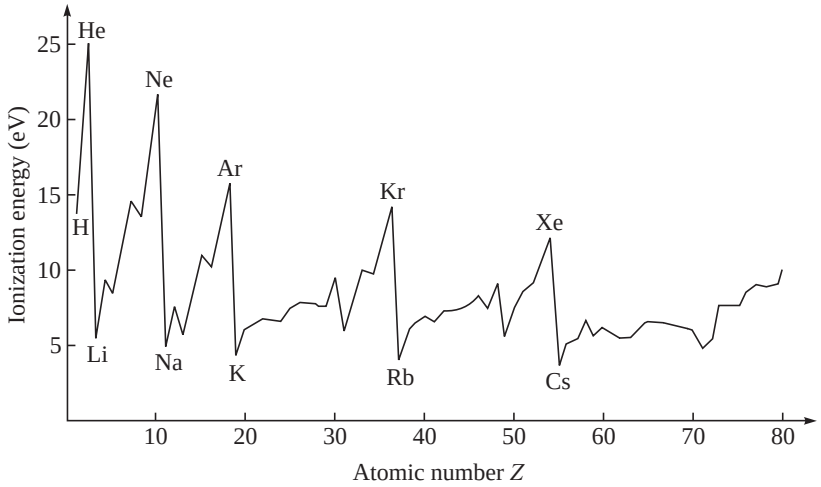


Figure 14.1 The ionization energy as a function of the atomic number Z.

This behaviour can be understood qualitatively as follows. In the case of alkali metals the single *s* electron is at a fairly large distance from the nucleus and is also shielded very effectively from the nucleus by the electrons in the completely filled subshells. As we move from group I to group VIII across a period, more and more electrons start filling the shell/subshell. These electrons have equivalent spatial distributions and so any one of them is not shielded very effectively from the nucleus by the other electrons. As a result the effective charge experienced by these electrons increases as Z increases during the filling of a subshell. Hence the binding energy reaches a maximum value for a closed subshell.

14.8 CORRECTIONS TO THE CENTRAL FIELD APPROXIMATION: *LS* COUPLING AND *jj* COUPLING

So far we have assumed that, in a many-electron atom, each electron moves independently in an average effective potential produced by the attraction of the nucleus and the repulsion due to the other electrons. This is called the *central field approximation*. It is necessary to apply corrections to this approximation so that a precise prediction of the energies, angular momenta and other properties of the various states of the atom may be possible. The two main corrections are those due to (a) the *residual electrostatic interaction* between the electrons and (b) the *spin-orbit interaction* of the electrons. The former is the difference between the actual electrostatic repulsion between the electrons and the average repulsion contained in the central field.

In all but the heaviest atoms, interaction (a) is much stronger than interaction (b). The procedure developed to take care of this situation is called the *LS (or Russel-Saunders) coupling scheme.* The second situation, in which (b) dominates (a), occurs in heavy atoms. It is taken care of by the *jj coupling scheme.*

LS Coupling

In this case the electrostatic interaction couples the individual orbital angular momenta $\mathbf{L}_i$ of all the electrons into a single resultant **L**. Similarly, the individual spin angular momenta $\mathbf{S}_i$ are coupled together into a resultant **S**. The weak spin-orbit interaction then couples **L** and **S** to give the total angular momentum of the atom **J**. Thus, the *LS* coupling scheme is

$$\boxed{\begin{array}{c}\mathbf{L} = \Sigma\mathbf{L}_i \\ \mathbf{S} = \Sigma\mathbf{S}_i \\ \mathbf{J} = \mathbf{L} + \mathbf{S} \\ \textbf{(LS Coupling)}\end{array}} \tag{14.11}$$

As explained in section 14.4, for a closed subshell $\mathbf{L} = \mathbf{S} = 0$ and so $\mathbf{J} = 0$. Therefore, only the electrons in the incomplete subshells need be considered to calculate **L**, **S** and **J** for the whole atom.

The **commonly used convention** in the spectroscopy literature is to use capital letters L, S, J, M_L, M_S and M_J for the quantum numbers pertaining to the whole atom in the case of many-electron atoms. We shall follow this convention.

The angular momentum magnitudes L^*, S^*, J^* and their respective z-components L_z, S_z, J_z can be expressed in terms of the corresponding quantum numbers L, S, J, M_L, M_S and M_J in the usual manner:

$$\boxed{\begin{array}{l}L^* = \sqrt{L(L+1)}\,\hbar;\ L_z = M_L\hbar \\ S^* = \sqrt{S(S+1)}\,\hbar;\ S_z = M_S\hbar \\ J^* = \sqrt{J(J+1)}\,\hbar;\ J_z = M_J\hbar\end{array}} \tag{14.12}$$

To obtain the possible values of L and S, we start with two electrons, find out all possible L, S values for these two electrons and then bring in the third electron, the fourth electron, and so on. For two electrons having quantum numbers l_1 and l_2, the allowed values of the orbital quantum number L are

$$L = |l_1 - l_2|,\ |l_1 - l_2| + 1,\ \ldots,\ l_1 + l_2 \tag{14.13}$$

Since $s_1 = s_2 = 1/2$, we have $S = 0,\ 1$.

For a particular L, S pair, the allowed values of J are

$$J = |l - s|,\ |l - s| + 1,\ \ldots,\ l + s - 1,\ l + s \tag{14.14}$$

The quantum states corresponding to definite values of *L*, *S* and *J* are called terms. For $S < L$, there are $(2S + 1)$ values of J. This number is called the *multiplicity* of the term. When $S > L$, there are $(2L + 1)$ values of J.

The *term notation* has been already discussed in detail in section 13.5. The reader should go back to it and review it before proceeding further. The term notation for the (L, S, J) state of a many-electron atom is

$$\boxed{{}^{2S+1}\mathscr{L}_J}$$

Some Examples of LS Coupling of Two Electrons

While determining the possible terms corresponding to a given configuration, we must remember to reject the values of L and S corresponding to states forbidden by the Pauli exclusion principle.

If the two electrons are *nonequivalent*, i.e., they belong to different subshells, then the exclusion principle is automatically satisfied. However, if the two electrons are *equivalent*, i.e., they belong to the same subshell, then the exclusion principle must be taken care of. It can be shown that according to the exclusion principle *only singlet states (S = 0) are allowed for even values of L and only triplet states (S = 1) are allowed for odd values of L*. We shall not go into the details of this rule.

EXAMPLE 1 Two nonequivalent *p* electrons (configuration *np n′p*)

Here $$l_1 = l_2 = 1;\ s_1 = s_2 = \frac{1}{2}$$

Therefore, the possible values of L and S are

$$L = 0, 1, 2;\ S = 0, 1$$

The J values for each L, S combination and the corresponding spectral terms are given in Table 14.4.

Table 14.4 *LS* Coupling of Two Nonequivalent *p* Electrons

L	*S*	*J*	*Spectral Terms*
0	0	0	$^1S_0$
0	1	1	$^3S_1$
1	0	1	$^1P_1$
1	1	0, 1, 2	$^3P_{0,1,2}$
2	0	2	$^1D_2$
2	1	1, 2, 3	$^3D_{1,2,3}$

Thus, there are a total of 10 possible terms.

EXAMPLE 2 Two equivalent *p* electrons (Configuration *np np*)

According to the rule given above, to satisfy the Pauli exclusion principle, we must exclude the second, the third and the sixth rows from Table 14.4. Thus there are only five allowed terms: $^1S_0$, $^3P_{0,1,2}$ and $^1D_2$.

EXAMPLE 3 Configuration *np n′d*

Here $$l_1 = 1,\ l_2 = 2;\ s_1 = s_2 = \frac{1}{2}$$

Possible values of $L = 1, 2, 3$

Possible values of $S = 0, 1$

The J values for each L, S combination and the corresponding spectral terms are given in Table 14.5.

Table 14.5 *LS* Coupling of Two Electrons having Configuration *np n′d*

L	*S*	*J*	*Spectral Terms*
1	0	1	$^1P_1$
1	1	0, 1, 2	$^3P_{0,1,2}$
2	0	2	$^1D_2$
2	1	1, 2, 3	$^3D_{1,2,3}$
3	0	3	$^1F_3$
3	1	2, 3, 4	$^3F_{2,3,4}$

Relative Energies of Different Terms. Hund's Rules

The relative energies of different terms can be obtained by detailed quantum mechanical calculation using perturbation theory. However, the following empirical rules, called *Hund's rules*, are useful in finding out the energywise ordering of the terms for the ground state configuration.

Rule 1: For a given configuration, the term with the largest possible value of *S* has the lowest energy. As *S* decreases the energy of the term increases.

Rule 2: For a given value of *S*, the term with the maximum value of *L* has the lowest energy.

Rule 3: For multiplets formed from equivalent electrons, the term with the smallest value of *J* has the lowest energy if the subshell is less than half-filled; the term with the highest value of *J* has the lowest energy if the subshell is more than half-filled. The multiplets in the first case are called *normal;* in the second case they are said to be *inverted.* There is *no* multiplet splitting if the subshell is just half-filled.

In Figures 14.2 and 14.3, we give the energywise ordering of the terms corresponding to the configurations discussed in Examples 1 and 2, respectively.

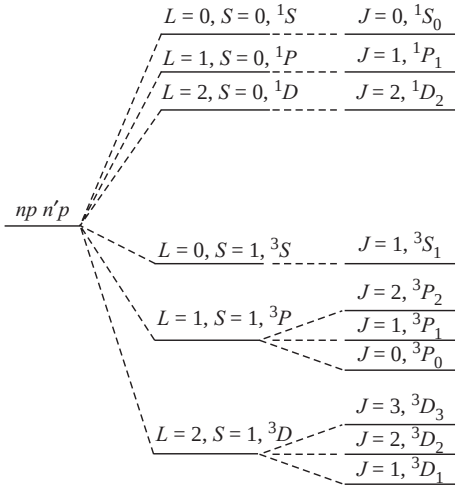


Figure 14.2 Energywise ordering of the terms for the configuration *np n′p*.

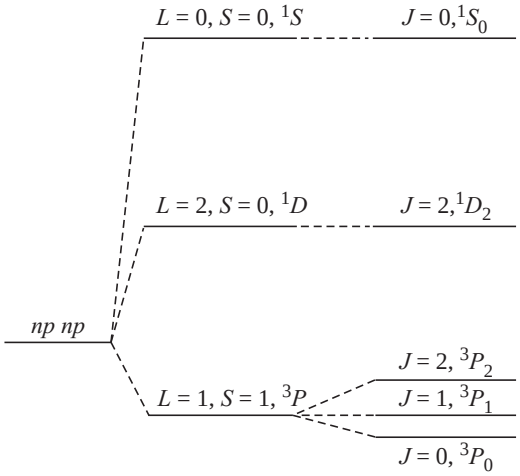


Figure 14.3 Energywise ordering of the terms for the configuration *np np*.

Selection Rules for Electron Transitions in LS Coupling

Assuming that only one electron makes a transition at a time, the selection rules for the transitions between *LS* coupled states are:

For the electron making the transition

(a) $\Delta l = \pm 1$
(b) $\Delta m_l = 0, \pm 1$

(14.15)

For the atom as a whole

(a) $\Delta S = 0$
(b) $\Delta L = 0, \pm 1$ ($L = 0 \leftrightarrow L' = 0$ forbidden)
(c) $\Delta M_L = 0, \pm 1$
(d) $\Delta J = 0, \pm 1$ ($J = 0 \leftrightarrow J' = 0$ forbidden)
(e) $\Delta M_J = 0, \pm 1$

(14.16)

jj Coupling

In heavy elements the spin-orbit interaction in individual electrons becomes large and dominates over the residual electrostatic interaction between electrons. Therefore, the $\mathbf{L}_i$ and $\mathbf{S}_i$ vectors of individual electrons couple to give resultant $\mathbf{J}_i$ vectors. These individual $\mathbf{J}_i$ vectors then combine to give a resultant $\mathbf{J}$ vector of the whole atom. This is called the *jj* coupling scheme:

$$\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i$$
$$\mathbf{J} = \Sigma \mathbf{J}_i$$
(*jj* Coupling) (14.17)

If there are two electrons having total angular momentum quantum numbers j_1 and j_2, then the possible values of the total angular momentum quantum number of the atom are

$$J = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 - 1, j_1 + j_2 \qquad (14.18)$$

In fact, one rarely finds examples of pure *jj* coupling. There is a gradual transition from *LS* to *jj* coupling in heavier atoms. However, *jj* coupling is of great importance in nuclear structure, because spin-orbit interaction is strong in nuclei.

Example: Two Nonequivalent p Electrons

For each electron

$$j_1 = j_2 = l \pm s = 1 \pm \frac{1}{2} = \frac{1}{2} \text{ or } \frac{3}{2}$$

The possible ways of combining these to obtain the J values and the spectral terms are given in Table 14.6.

Table 14.6 *jj* Coupling of Two Nonequivalent *p* Electrons

j_1	j_2	J	Spectral Terms
$\frac{1}{2}$	$\frac{1}{2}$	1, 0	$\left(\frac{1}{2}, \frac{1}{2}\right)_{1,0}$
$\frac{3}{2}$	$\frac{1}{2}$	2, 1	$\left(\frac{3}{2}, \frac{1}{2}\right)_{2,1}$
$\frac{1}{2}$	$\frac{3}{2}$	2, 1	$\left(\frac{3}{2}, \frac{1}{2}\right)_{2,1}$
$\frac{3}{2}$	$\frac{3}{2}$	3, 2, 1, 0	$\left(\frac{3}{2}, \frac{3}{2}\right)_{3,2,1,0}$

There are a total of 10 terms.

SUMMARY

1. The Schrödinger equation for a many-electron atom cannot be solved exactly due to the mathematical complexities of handling the interaction of electrons with one another.
2. As a first approximation, it is assumed that each electron moves in an effective spherically symmetric potential $V(r)$ generated by all the other electrons and the nucleus. This is called the central field approximation. The energy of a state now depends on both n and l rather than just on n. However, the dependence on l is rather small. A quantum state is still labelled by the quantum numbers (n, l, m_l, m_s). There is no dependence on m_l and m_s.

3. The distribution of electrons in these states in the ground state of the atom is governed by the Pauli exclusion principle, which states that: No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).

4. A consequence of the exclusion principle is that the wave function for a many-electron system must be antisymmetric in the exchange of any two electrons. For a two-electron system

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1) & \psi_b(1) \\ \psi_a(2) & \psi_b(2) \end{vmatrix}$$

5. The Pauli exclusion principle leads to atomic shell structure. The electronic states having the same value of n are said to belong to the same shell. In a shell the states having the same value of l are said to belong to the same subshell. A subshell is denoted by the (n, l) values, such as 1s, 2s, 2p etc. The maximum number of electrons in a subshell is $2(2l + 1)$ and the maximum number of electrons in a shell is $2n^2$.

6. A specification of the n and l values for all the electrons in an atom is called the electronic configuration for that atom.

7. The order of succession of the energy levels E_{nl} is nearly the same for all atoms. It is 1s, 2s, 2p, 3s, 3p, [4s, 3d], 4p, [5s, 4d], 5p, [6s, 4f, 5d], 6p, [7s, 5f, 6d].

8. The electronic shell structure of elements accounts for the periodicity and regularity in their properties which was systematically studied by the chemists. According to the periodic law given by Mendeleev: When the elements are arranged in order of increasing atomic number, the elements with similar physical and chemical properties recur at regular intervals. The quantum theory tells us that this is a consequence of the regularities in the electronic configuration of outer electronic (valence) subshells and the energy gap between the valence subshell and the next one.

9. There are two main corrections to the central field approximation. These are due to (a) the residual electrostatic interaction between the electrons and (b) the spin-orbit interactions of the electrons. In all but the heaviest atoms, the former is dominant, leading to *LS* coupling. The opposite situation leads to *jj* coupling.

QUESTIONS

1. What is central field approximation in the context of many-electron atoms?

2. State and explain the Pauli exclusion principle.

3. (a) What are symmetric and antisymmetric wave functions? What is Slater determinant?

(b) Explain how antisymmetry of the two-electron wave function leads to the Pauli exclusion principle.

4. State the generalized Pauli principle.
5. Discuss briefly the atomic shell structure, explaining the meaning of shells and subshells. What is meant by electronic configuration of atoms?
6. Discuss how the electronic shell structure of elements explains the periodic table and the ionization energies of elements.
7. Discuss what is meant by *LS* coupling and *jj* coupling. State the selection rules for *LS* coupling.
8. State Hund's rules.
9. Distinguish between singlet and triplet states in the case of atoms which have two electrons in the outermost subshell. Which of the two states has lower energy?

EXERCISES

1. Find the *S*, *L* and *J* values that correspond to each of the following states:

$$^2S_{1/2},\ ^1S_0,\ ^3P_2,\ ^2D_{3/2},\ ^5F_5,\ ^2P_{3/2}$$

2. Consider a two-electron system with $l_1 = 2$ and $l_2 = 1$. What are the possible total angular momentum (J) states, assuming *LS* coupling. Write the spectral term for each state.

[**Hint.** See Example 3 of *LS* coupling in the text]

3. Find the possible values of total angular momentum quantum number J in *LS* coupling of two atomic electrons having orbital quantum numbers
   (a) $l_1 = 1$ and $l_2 = 3$,
   (b) $l_1 = 2$ and $l_2 = 3$.
4. The electronic configuration of Mg is $1s^2\ 2s^2\ 2p^6\ 3s^2$. Obtain its spectral term. [***Ans.*** $^1S_0$]

Appendix

A The Fourier Transform

Consider a single-valued periodic function $f(x)$, with period $2L$, so that

$$f(x + 2L) = f(x) \tag{A.1}$$

If $f(x)$ and $f'(x)$ are piecewise continuous, then it can be expanded in a Fourier series in the interval $(-L, L)$. The series has the form

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left(a_n \cos\frac{n\pi x}{L} + b_n \sin\frac{n\pi x}{L} \right) \tag{A.2}$$

where the coefficients a_n and b_n are given by

$$a_n = \frac{1}{L} \int_{-L}^{L} f(x) \cos \frac{n\pi x}{L} dx, \qquad n = 0, 1, 2, \ldots \tag{A.3}$$

and

$$b_n = \frac{1}{L} \int_{-L}^{L} f(x) \sin \frac{n\pi x}{L} dx, \qquad n = 1, 2, \ldots \tag{A.4}$$

Since

$$\cos\frac{n\pi x}{L} = \frac{1}{2} \left(e^{in\pi x/L} + e^{-in\pi x/L}\right)$$

and

$$\sin\frac{n\pi x}{L} = \frac{1}{2i} \left(e^{in\pi x/L} - e^{-in\pi x/L}\right)$$

We can write the Fourier series in the form

$$f(x) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} c_n \, e^{in\pi x/L} \tag{A.5}$$

The factor $1/\sqrt{2\pi}$ has been put so that the final formulae are in symmetrical form. The coefficients c_n are given by

$$c_n = \frac{1}{L}\sqrt{\frac{\pi}{2}}\int_{-L}^{L} f(x)\, e^{-in\pi x/L}\, dx \tag{A.6}$$

Let us now rewrite (A.5) as

$$f(x) = \frac{1}{\sqrt{2\pi}}\sum_{n=-\infty}^{\infty} c_n\, e^{in\pi x/L}\, \Delta n \tag{A.7}$$

where Δn is the difference between two successive integers, which is unity.

Suppose now that the function $f(x)$ is not periodic. We may say that the period is infinite. We shall see, by taking the limit $L \to \infty$, that in this case the Fourier series (A.7) changes into an integral. As L increases, the difference between the successive terms in the series (A.7) becomes smaller and smaller. Recalling the Riemann definition of an integral, we can replace the sum over n by an integral:

$$f(x) = \frac{1}{\sqrt{2\pi}}\sum_{-\infty}^{\infty} c_n\, e^{in\pi x/L}\, dn \tag{A.8}$$

Let us introduce a new variable k:

$$k = \frac{n\pi}{L} \tag{A.9}$$

and define a new function $A(k)$:

$$A(k) = \frac{Lc_n}{\pi} \tag{A.10}$$

We have

$$dn = \frac{L}{\pi}dk, \quad c_n = \frac{\pi}{L}A(k)$$

Substituting in (A.8)

$$\boxed{f(x) = \frac{1}{\sqrt{2\pi}}\int A(k)\, e^{ikx}\, dk} \tag{A.11}$$

Taking the limit $L \to \infty$ in (A.6) and substituting in (A.10), we get

$$\boxed{A(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(x)\, e^{-ikx}\, dx} \tag{A.12}$$

The integrals (A.11) and (A.12) are called *Fourier integrals*. The function $A(k)$ is known as the *Fourier transform* of $f(x)$ and the function $f(x)$ is known as the *inverse Fourier transform* of $A(k)$.

Appendix

B The Dirac Delta Function

The reader is familiar with the Kronecker delta δ_{ij} which is defined for the discrete variables i and j as

$$\begin{aligned} \delta_{ij} &= 0 \qquad \text{if } i \neq j \\ &= 1 \qquad \text{if } i = j \end{aligned} \tag{B.1}$$

Equivalently, δ_{ij} may be defined by

$$f(j) = \sum_{i=1}^{\infty} \delta_{ij}\, f(i), \qquad j = 1, 2, \ldots \tag{B.2}$$

The Dirac delta function is a generalization of the Kronecker delta to the case of a continuous variable. It is defined by the equations

$$\delta(x - a) = 0 \qquad \text{if } x \neq a \tag{B.3}$$

$$\text{and} \quad \int_{-\infty}^{\infty} \delta(x - a)\, dx = 1 \tag{B.4}$$

Equivalently, if $f(x)$ is an arbitrary function, then

$$\int_{-\infty}^{\infty} f(x)\, \delta(x - a)\, dx = f(a) \tag{B.5}$$

In particular, for $a = 0$,

$$\delta(x) = 0 \qquad \text{if } x \neq 0 \tag{B.6}$$

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1 \tag{B.7}$$

and

$$\int_{-\infty}^{\infty} f(x)\, \delta(x)\, dx = f(0) \tag{B.8}$$

It is clear that $\delta(x)$ is not a proper function of x and is exceedingly singular in nature. Qualitatively, it may be thought of as being zero everywhere except at $x = 0$, and being so large at $x = 0$ that the area between it and the x-axis is unity.

Properties of Delta Function

Below we give the main properties of the delta function. These properties have meaning only if a subsequent integration is carried out:

$$\left.\begin{array}{ll}
1. & \delta(x) = \delta(-x) \\
2. & x\delta(x) = 0 \\
3. & \delta'(x) = -\delta'(-x) \\
4. & x\delta'(x) = -\delta(x) \\
5. & \delta(ax) = \dfrac{1}{|a|}\,\delta(x),\ a \neq 0 \\
6. & f(x)\,\delta(x-a) = f(a)\,\delta(x-a) \\
7. & \displaystyle\int \delta(a-x)\,\delta(x-b)\,dx = \delta(a-b) \\
8. & \delta(x^2-a^2) = \dfrac{1}{2|a|}\,[\delta(x-a)+\delta(x+a)] \\
9. & \delta[(x-a)(x-b)] = \dfrac{1}{|a-b|}\,[\delta(x-a)+\delta(x-b)],\ a \neq b
\end{array}\right\} \quad \text{(B.9)}$$

Integral Representation of the Delta Function

It is possible to obtain an integral representation of the Dirac delta function using Fourier integrals. Substituting $A(k)$ given by (A.12) into (A.11), we get

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty} f(x')\,e^{-ikx'}\,dx'\right]\,e^{ikx}\,dk$$

Reversing the order of integration,

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(x')\left[\int_{-\infty}^{\infty} e^{ik(x-x')}\,dk\right]\,dx' \qquad \text{(B.10)}$$

Comparing (B.10) with (B.5), we obtain

$$\boxed{\delta(x-x') = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ik(x-x')}\,dk} \qquad \text{(B.11)}$$

This is the integral representation of the Dirac delta function. It is very useful in quantum mechanics and has been used in chapter 6 in normalizing the momentum eigenfunctions (see Equation 6.97).

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